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13. ABSTRACT (Maximum 200 words)

The discovery, study, and eventual remediation of pollution that threatens water resources are very important in maintaining the health of the environment and people. However, the discovery of many types of pollution is often difficult. This project focuses on a method used to discover hidden contamination -- soil gas surveying.

The Rose-Hulman Institute of Technology campus in Terre Haute, Indiana is on the site of an old farm. The campus has an old gasoline station on its border, a chemical storage building on the grounds, and areas where fuel, oil, and solvents are used and stored by the physical plant operation. There was a possibility that underground contamination might be present from these operations.

Contaminants typical of these types of operations include Benzene, Toluene, Ethylbenzene, and m, p, and o - Xylenes. Using the first letter of these contaminants produces the acronym BTEX. BTEX, chemicals used in the processing of petroleum products and other manufacturing. Other contaminants common in these types of operations include chlorinated solvents such as Trichloroethylene and Tetrachloroethylene. These are important not only because of the high possibility of their existence but also their high toxicity.

No significant areas of contamination were found for the contaminants tested. A detailed description of the method and results of testing are presented. Recommendations for improved management of potential contamination areas are also presented.

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**SOIL GAS SURVEY AND ANALYSIS OF THE ROSE-HULMAN INSTITUTE OF  
TECHNOLOGY CAMPUS USING A PORTABLE GAS CHROMATOGRAPH**

**A Thesis**

**Submitted to the Faculty**

**of**

**Rose-Hulman Institute of Technology**

**by**

**Harvey Baxter Jones III**

**In Partial Fulfillment of the**

**Requirements for the Degree**

**of**

**Master of Science in Environmental Engineering**

**May 1996**

I dedicate this work to my family, Sherry, Ashley, and Kyle.  
Without their support this thesis would not have been possible.

## ACKNOWLEDGMENTS

A great many people assisted me in the completion of this work; and I am therefore in deep gratitude to them. First, I would like to thank my advisor, Dr. Martin J. Thomas, for his instruction, mentoring, and support in the completion of my thesis. I would also like to thank Dr. Robert J. Houghtalen, Dr. Dale S. Bremmer, Dr. J.D. Gibson, and Dr. Sharon Jones whose instruction and expertise were also instrumental in my work. I would be remiss if neglected to thank the outstanding support staff at Rose-Hulman. Namely, I would like to thank Keith Royer and Frank Cunning who assisted in the design and completion of my sampling apparatus; Menka Neal who kept me on track with graduation requirements; Jack Bagley who provided his expertise in print and layout; and John Robson and Margaret Ying who provided style insight and research assistance. Finally, I would like to thank Dr. Samuel Hulbert who ensured I received the funds I needed to complete the course work culminating with this thesis.

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## 1. INTRODUCTION

### 1.1. SCOPE OF THE THESIS

The earth is becoming a very crowded place. Human beings are heavily populating the world as evidenced by our 1994 population of over 5.6 billion. This is particularly alarming in that the 1980 population was under 4.5 billion; and the 2010 projection is over 7 billion [1]. As a result, the planet's resources are being depleted at an astounding rate. Because we cannot use most resources at one-hundred percent efficiency, an additional problem is created -- pollution.

We pollute all media: air, water, and soil. Damage often occurs to such an extent that the media in a polluted area can become unavailable for some users for years. We attempt to preserve these resources by passing laws such as the Resource Conservation and Recovery Act of 1976 (RCRA) and the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA, or more commonly known as "Superfund"). RCRA was created to regulate current practices and CERCLA to facilitate the cleanup of our past indiscretions.

New or improved technologies to aid in cleanup have and are being developed today at a faster rate than ever before. One such technology is portable gas chromatography, the focus of this thesis.

The present project uses portable gas chromatography to conduct a soil gas survey of the Rose-Hulman Institute of Technology campus in Terre Haute, Indiana. The survey was designed to detect man-made volatile organic compounds (VOCs) that might be found in the area. The research also includes information on liability issues, remediation options, and associated costs.

## 1.2. STATEMENT OF PROBLEM

The potable water supply in the United States is approximately 81% surface water and 19% groundwater [2: 146]. During periods of drought surface water is solely supplied by groundwater. With these facts in mind, it is important to protect the groundwater and to remediate any contaminants that might pose a threat to the groundwater supply.

Many methods, termed best management practices, or BMPs, are available to accomplish this end. One particularly effective BMP, the soil gas survey, is a method by which the engineer can monitor and locate contaminated areas.

The Rose-Hulman Institute of Technology campus was used as a site to develop and demonstrate a soil gas surveying methodology. Prior to being the grounds for an academic institution, the campus was a working farm. It is possible there might have been contamination from the old farming operation.

Additionally, the campus has a gas station on its southeast border. Though the station appears to comply with all state and national regulations, it was constructed on the exact site as a previous station. It is possible that there was contamination from one of the in-ground fuel tanks. Contamination could have occurred during the operation, excavation, or installment of the old or new tanks. The campus also conducts physical plant operations that involve an above ground fuel tank, the use of solvents, and the use of other petroleum products, all possible sources of contamination. The campus has a chemical storage facility for use by the Chemistry and Chemical Engineering Departments. Though the likelihood for contamination from that source is low due to excellent management practices, it is, nonetheless, a concern since volatile organic compounds are stored there. Finally, the institute hosts a huge bonfire each year in celebration of homecoming. Materials used for this event include old railroad ties and pallets from local companies who often use solvents in their industrial processes. These could pose a contamination threat.

A soil gas survey on the Rose-Hulman campus can identify the possibility of contamination to the local soil and groundwater supply.

### 1.3. GAS CHROMATOGRAPHY

A gas chromatograph is an instrument used to identify compounds in a gaseous state. The gas chromatograph allows for the input of a sample through an inlet port (pumped stream or syringe injection) into a carrier gas (pure air, hydrogen, helium, or nitrogen) which transports the substance through the instrument. The sample then passes through a length of glass, metal, or teflon tubing. This tubing, known as the column, is where the subcomponents separate by distinct time increments due to varying retention times in the column. The sample then passes through a chemical or physical detection device where the response of the detector is fed into a recorder. Components of the sample are identified by matching retention times with known substances. Finally, the sample exits the system (see Figure 1-1).

#### 1.3.1. Sample Injection

Two methods exist to introduce samples into the gas chromatograph:

1. Loop injection -- the method where the analyst allows the gas chromatograph to pump samples into itself. This is a particularly useful method when numerous samples are required to be analyzed at a particular site. Examples where this might be most useful are air monitoring or soil gas monitoring at a fixed location, and;
2. Syringe injection -- the method where the analyst uses a gas tight syringe to capture and inject a sample into the gas chromatograph. This is particularly useful when conducting small numbers of samples at multiple sites, as is the case in soil gas surveying.

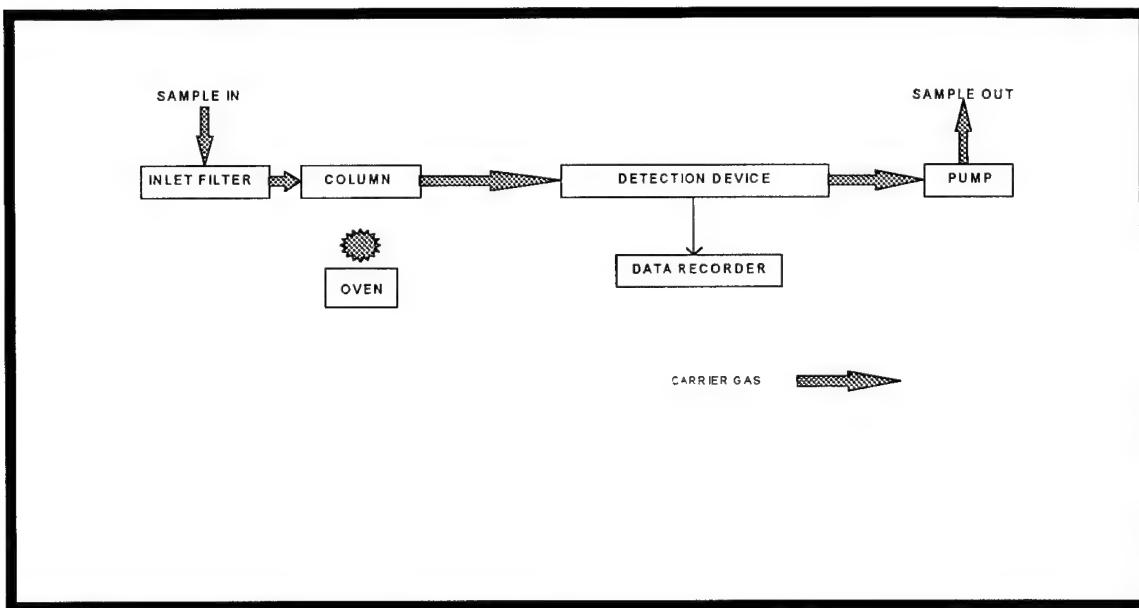


Figure 1-1  
Gas Chromatograph Block Diagram [3: 186]

### 1.3.2. Column Types

Two general types of columns exist:

1. Unpacked columns -- a column constructed strictly of tubing where the physical properties of the substances in the sample and their interaction with the tubing walls cause their separation into different time intervals, and;
2. Packed columns -- a column where the tubing has been packed with an inert material, fiberglass as an example, impregnated with a nonvolatile liquid, silicone oil or polyethylene glycol as examples, to aid in distinguishing between compounds that show little or no difference in retention times in an unpacked column. For instance, m and p xylenes are indistinguishable in an unpacked column, but may be identified separately with a special packed column).

### 1.3.3. Retention Time

Retention volume ( $V_R$ ), (the volume of gas required to carry a component through a column) is related to retention time ( $t_R$ ), by

$$V_R = t_R F_c$$

where  $F_c$  is the volume flow rate of the gas at the outlet. This can also be corrected for average pressure in the column as follows

$$V_R^0 = j t_R F_c$$

where

$$j = 3[(p/p_o)^2 - 1] / 2[(p/p_o)^3 - 1]$$

and  $p_i$  and  $p_o$  are the gas pressures at the inlet and outlet of the column respectively.

The retardation factor ( $R_F$ ) is the rate of movement of a component peak in the column compared with the rate of movement of the carrier gas. For a column length  $l$

$$R_F = l/t_R / l/t_G = t_R/t_G$$

where  $t_G$  is the retention time of the carrier gas [4: 806].

### 1.3.4. Oven

The oven is the component that raises and maintains the temperature of the column at or above ambient so that the reaction will be steady state. Set temperatures vary depending on ambient temperatures, capability of the gas chromatograph, and requirements to differentiate between different compounds. Higher temperatures lower retention times leaving less time between peaks. High temperatures may be desirable to speed up analysis time, or undesirable if peaks are close to one another in time sequence causing overlap of peaks.

### 1.3.5 Detection Devices

Many types of detection devices are used to record the presence of compounds in a given sample using chemical or physical properties of the compounds. These include:

1. Electron Capture Detectors -- Electron capture detectors measure how well compounds with halogen atoms or polar functional groups accept beta particles (electrons) from

a radioactive source such as tritium. This technique is particularly useful in identifying pesticides, trihalomethanes, and chlorinated solvents;

2. Thermal Conductivity Detectors -- Thermal conductivity detectors measure a compound's ability to carry heat away from a wire heat source. As a sample passes the heat source, the temperature changes. This results in a change in resistance in the wire, thus a change in electrical response that is then recorded. This method is particularly useful in measuring the gases produced during anaerobic digestion such as methane;

3. Flame Ionization Detectors -- Flame ionization detectors measure the ability of a compound to conduct an electrical charge after being burned. As a compound burns, it releases ions and electrons. An electric current passes through the particles and the ability of the material to conduct the charge is measured. This method is particularly useful in detecting organic acids and hydrocarbons, and;

4. Photoionization Detectors -- Photoionization detectors, similar to flame ionization, also measure a compound's ability to conduct an electrical charge. However, it uses photons from ultra violet light (105 to 150 nm range)[5: 428] to ionize the compounds.

#### **1.3.6. Chromatograms**

The output from a gas chromatograph is a chromatogram. The chromatogram is a plot of the electrical response of the sample over time. A typical chromatogram is pictured in Figure 1-2.

#### **1.3.7. Determination of Contaminant Concentration**

The analyst uses the chromatogram to determine the concentration of material by comparing the area of the peak (in electric potential multiplied by the elapsed time such as an area of mVs) with the area produced by a known concentration of compound.

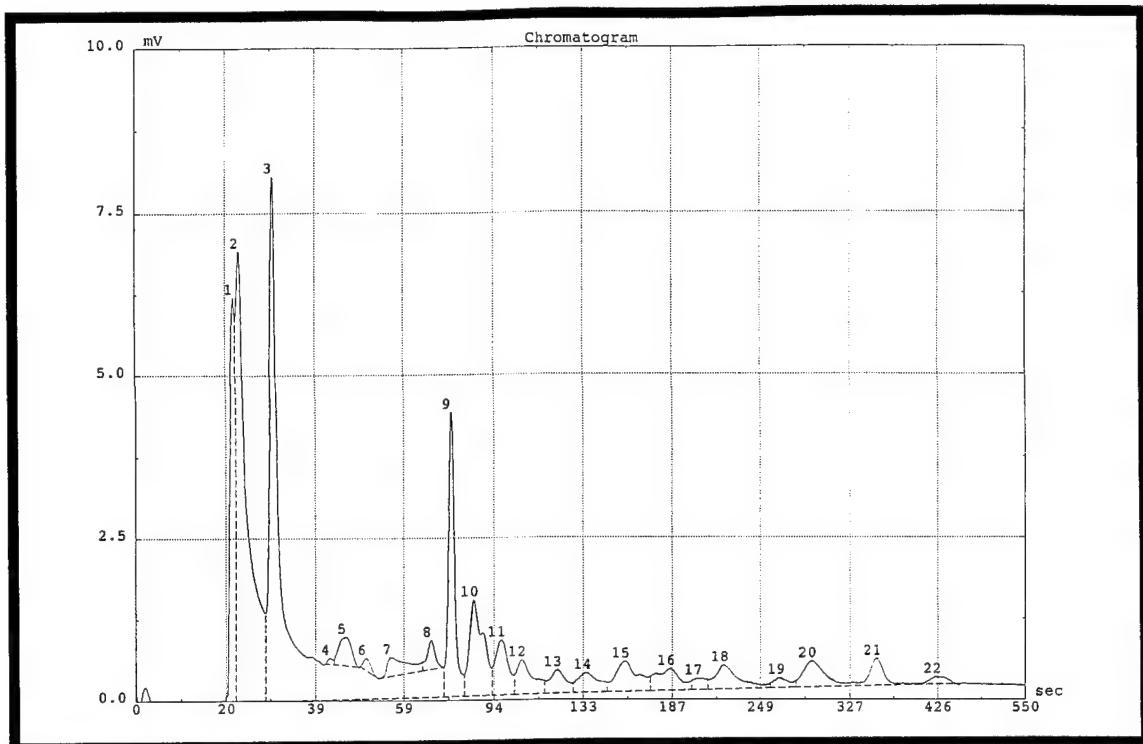


Figure 1-2

**Sample Chromatogram**

(Each numbered peak corresponds to a different compound in the sample)

**1.4. SOIL GAS SURVEYS**

A soil gas survey is a systematic method of sampling, analyzing, and interpretation of soil gases under a site [9: 86]. The surveys are designed to include sampling of all areas of interest. Areas of interest are defined as locations where there is good cause to believe that surface and/or subsurface contamination may exist such as known spill areas, underground storage tank locations, past or present areas where target contaminants were used, etc.

**1.4.1. Soil Gas**

All soils contain intergranular voids that are either filled with fluid or gas. This gas in these voids is the soil gas.

#### 1.4.2. Site Coverage

Equal coverage can be assigned by laying out the sample sites on a uniform grid. Enough samples must be taken in areas of known contamination to ensure sufficient detail for mapping purposes. For instance, the grid around a small building or small area of concentration (say 10,000 ft<sup>2</sup>) might be in 10ft increments and offset between rows. A medium sized site (larger than a small site but no larger than 3 acres) might be in 15yd increments and again offset between rows. The most important point is that the number of samples must be representative of the area being surveyed and requires some engineering judgment to be utilized. See Figure 1-3.

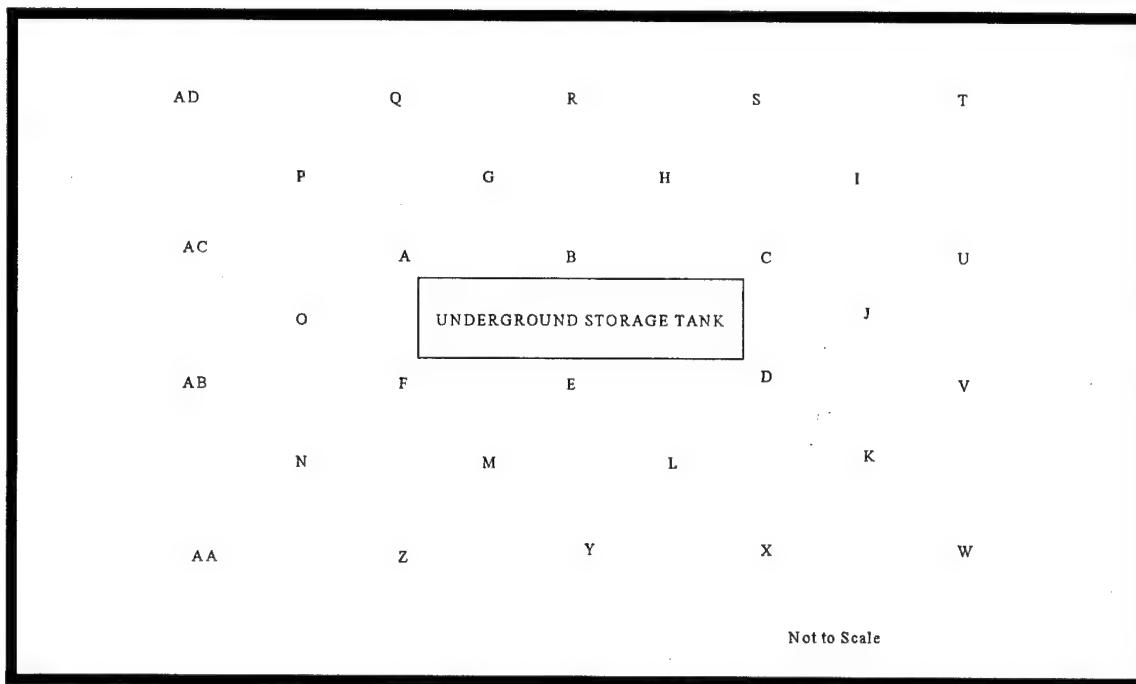


Figure 1-3

#### Example Site Coverage Map

(Note: alpha numeric designations represent sample collection sites)

### **1.4.3. Sampling Methods**

The two basic methods of sampling are:

1. Active sampling - Active sampling is accomplished by drawing an instant sample for analysis. In active methods, shallow driven probes (3 - 6 feet) are used to enable the pumping of gas directly into an analysis device. A sample collection depth of at least 4 feet avoids surface desorption and microbial degradation [10]. Alternately, samples may be pumped into a storage bag or stainless steel or glass container for analysis at a later time [11: 79]. The advantages of this method are immediate results, little site disturbance, and small sample degradation because little time is lost between sampling and analysis. The disadvantage is that the analyst must remain on site during the entire sampling period; and
2. Passive sampling - Passive sampling is accomplished by using devices to accumulate gases over a period of time prior to analysis. In this method devices are buried in the ground and retrieved later for analysis. The advantage of this method is that there is no requirement for the analyst to remain constantly at the site. The disadvantage of this method is the requirement for much more site disturbance than active sampling due to size of the sample accumulator. In addition; the concentrations of compounds that volatize quickly may be negatively affected by the long analysis turnaround time required.

### **1.4.4. Analysis**

Analysis includes methods such as detector tubes and gas chromatography. Detector tubes are hand-held, semiquantitative, glass devices that change color in the presence of the target compound. These tubes are available for over 200 compounds at a variety of concentration ranges [12]. Though simple to use, they do not produce high quantitative accuracy. Portable gas chromatographs can provide high quantitative accuracy, contamination identification, and rapid response.

### 1.5. OBJECTIVE

The objective of this research was to conduct a soil gas survey of the Rose-Hulman Institute of Technology campus (see Figure 1-4) using portable gas chromatography in order to identify areas of volatile organic compound contamination. Areas on campus that were most likely to have contamination of this type were selected for sampling. Compounds that are commonly found at Superfund sites (Table 1-1) and in gasoline that are easily detectable by gas chromatography were selected. The list includes benzene, toluene, ethylbenzene, m, o, and p -- xylenes (using the first letter of these compounds produces the acronym "BTEX"), trichloroethylene, and tetrachloroethylene. This research was to be followed up by:

- detailed concentration maps of contaminated areas (if necessary),
- a discussion of liability issues,
- a discussion of remediation options,
- an estimated cost of the cleanup (if necessary), and
- conclusions and recommendations.

**Table 1-1**  
**Most Frequently Identified Substances Detectable**  
**by Soil-Gas Sampling at 546 Superfund Sites [8: 741]**

Compound	Percent of Sites
Trichloroethylene	33
Toluene	28
Benzene	26
Chloroform	20
Tetrachloroethylene	16
1,1,1-Trichloroethane	14
Ethylbenzene	13
Xylenes	13
Methylene Chloride	12
trans-1,2-Dichloroethylene	11



Figure 1-3

**Rose-Hulman Campus Map**

## **2. SAMPLE COLLECTION PROCEDURE**

The U.S. Environmental Protection Agency Standard Operating Procedure #2149 (Soil Gas Sampling) was used as the base document for this procedure. The procedure was modified based on suggestions received from Dr. Thomas M. Spittler, Director, U.S. Environmental Protection Agency Region I Laboratory [10].

### **2.1. METHOD SUMMARY**

#### **2.1.1. General Sampling (see Figure 2-1)**

A 3/8 - inch diameter hole is driven into the ground to a depth of 4 feet using a slam bar (see Figure 2-2 and 2-3). A 1/4 - inch outside diameter (O.D.) stainless steel probe is inserted into the vacated hole. The hole is then sealed at the top around the probe using modeling clay (see Figure 2-4). The gas contained in the interstitial spaces of the soil is sampled by pulling the gas through the probe with a commercial air sampling pump. Prior to the gas reaching the pump, a sample is withdrawn from the stream with a gas microsyringe. The sample is then injected immediately into a Photovac 10Splus portable gas chromatograph for immediate analysis.

#### **2.1.2. Vacuum Air Sampling**

No commercial air sampling pumps were available for this project, so a vacuum was used instead. The vacuum is a Wangenstein Suction System by Phelan Manufacturing Corporation of Minneapolis, Minnesota (see Figure 2-5). The vacuum is a hand operated apparatus capable of approximately 20 inches of mercury. Air is evacuated by using the hand pump and flow into the container is controlled with an adjustable air flow meter. The adjustable air flow meter has a range of flow from 0 to 2.5 cubic feet per hour (1180 cubic centimeters per

minute). Though the vacuum was designed for hospital use, it performs well for soil gas sampling.

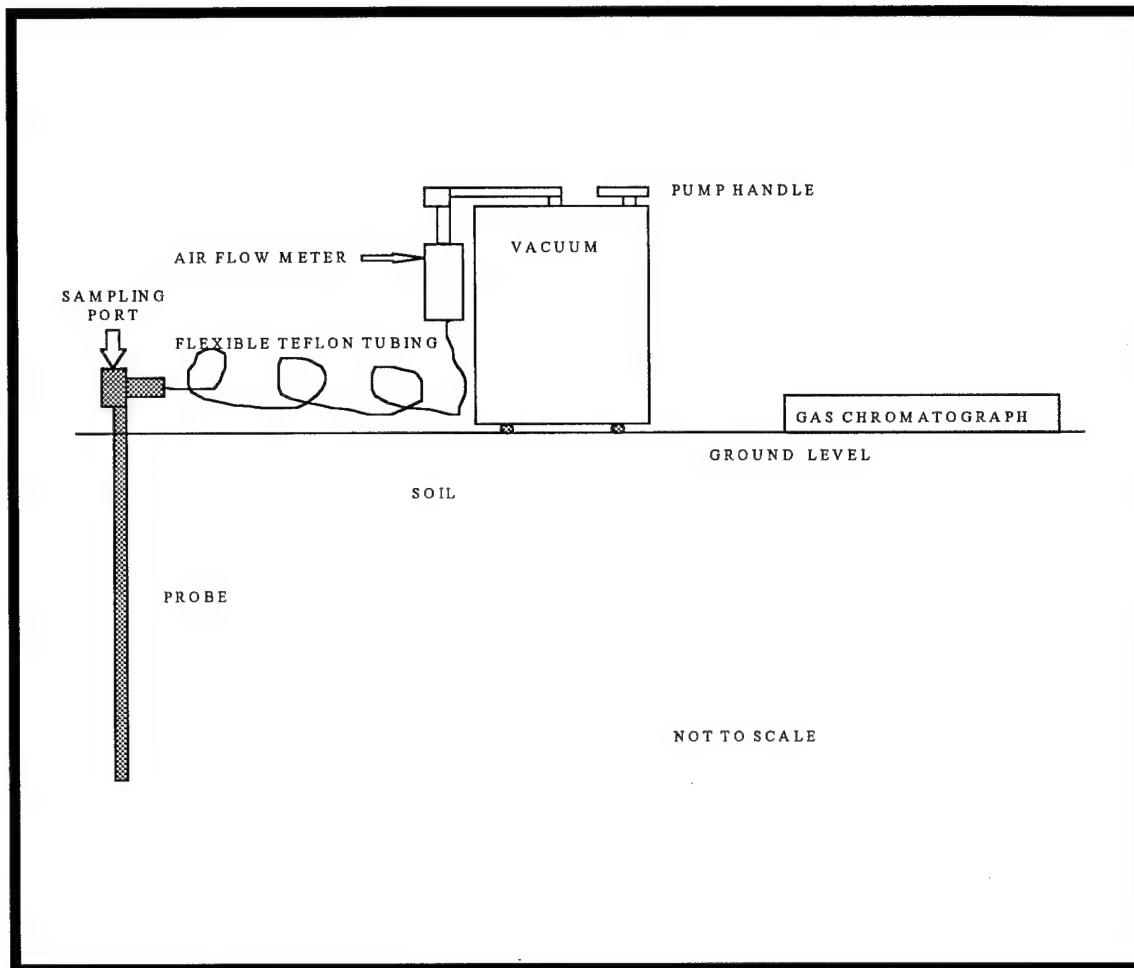


Figure 2-1  
Sample Collection Schematic

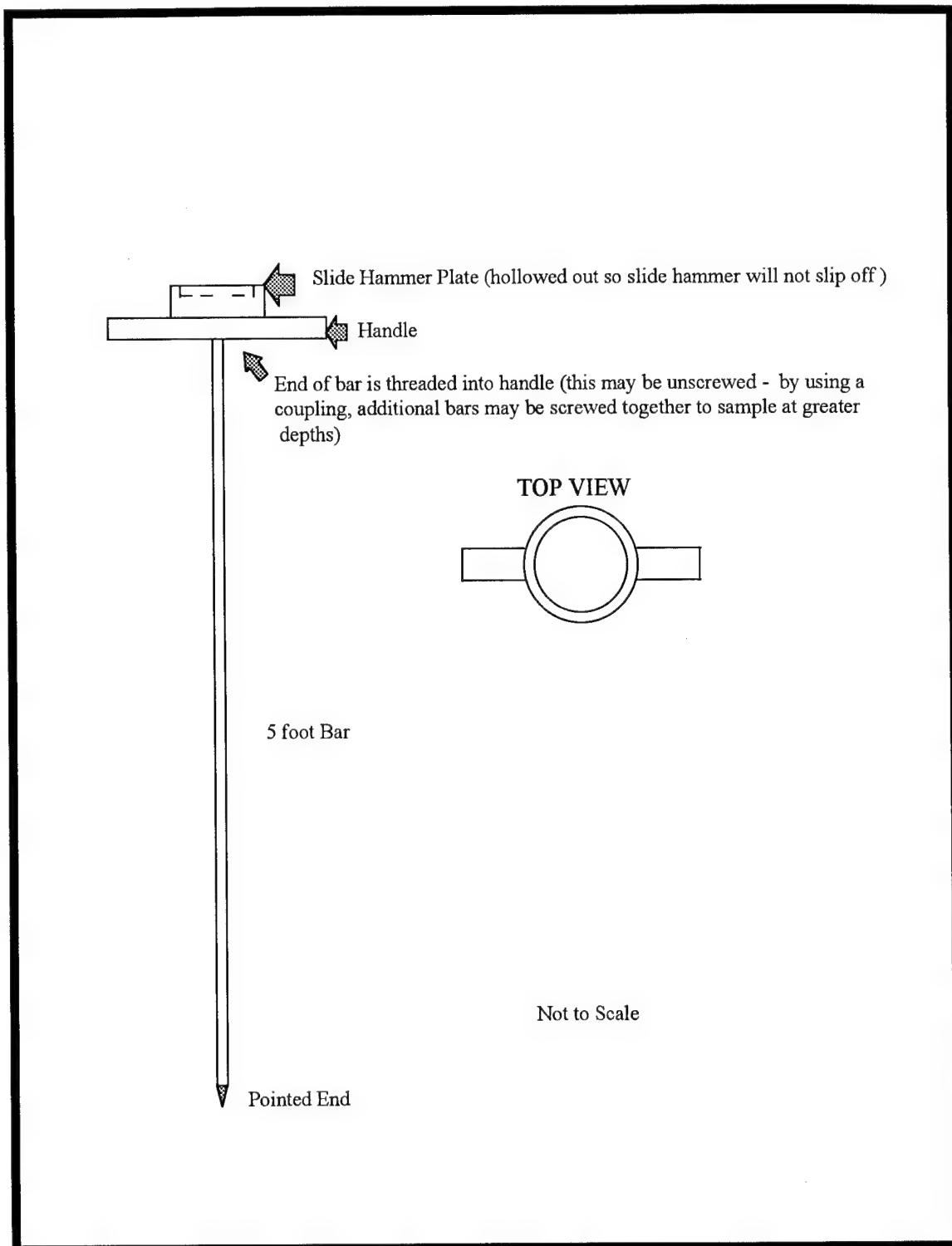


Figure 2-2

**Slam Bar**



Figure 2-3

**Slam Bar Driven into the Ground**

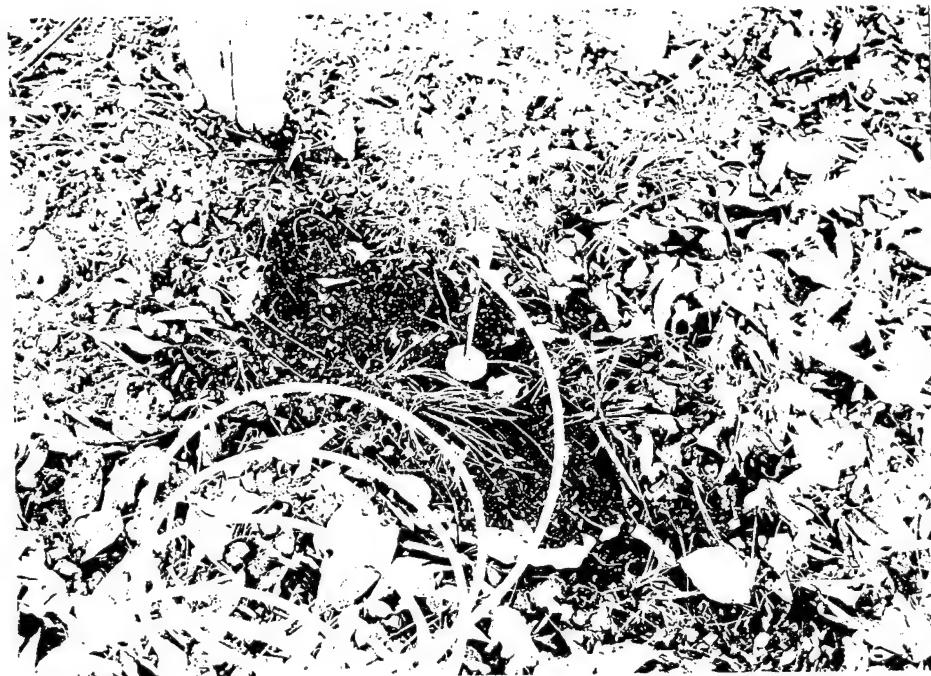


Figure 2-4

**Emplaced Probe**

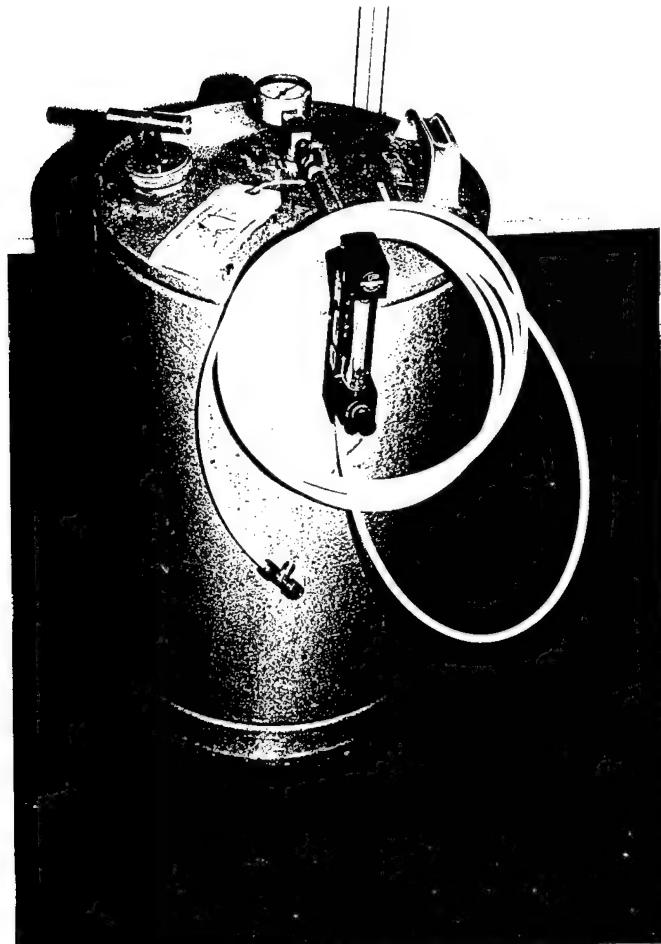


Figure 2-5  
Sample Vacuum System

## 2.2. SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Since the sample is drawn directly from the gas stream with a syringe and immediately injected into the gas chromatograph, no preservation, containers, handling, or storage should be necessary. If, however, a sample is to be taken for further analysis, see section 3.3 in U.S. Environmental Protection Agency Standard Operating Procedure #2149. Examples of storage devices include Tedlar bags, Tenax tubes, and Summa canisters.

## **2.3. INTERFERENCES AND POTENTIAL PROBLEMS**

### **2.3.1. Site Geology**

Certain site geological features create soil gas sampling difficulties. A high water table may contaminate samples with water. Water cannot be introduced into the gas chromatograph. An impermeable layer (clay or slag) between the end of the sampling probe and the area of contamination may produce false contaminant concentrations. Insufficient porosity in the soil may make it difficult to establish a continuous stream for sampling.

### **2.3.2. Probe Clogging**

The probe should have a removable wire placed within it so the wire may be used, if necessary, to unclog the end of the probe if it becomes clogged with soil during placement.

### **2.3.3. Underground Utilities**

The study of underground utility maps is required prior to emplacing holes to avoid injury. Electrical, sewage, natural gas, cable television, and water are examples of utilities to be aware of. Each sample site should also be screened with a metal detector prior to installation.

## **2.4. EQUIPMENT/APPARATUS**

The method described here is a slam bar method. The power hammer method may also be utilized (see section 3.5.2 of U.S. Environmental Protection Agency Standard Operating Procedure #2149 for details). The equipment required includes:

- slam bar (see Figure 2-2),
- soil gas probes, stainless steel tubing, 1/4 inch O.D., 4 foot length [10],
- flexible wire or cable used for clearing the tubing during insertion into the well,
- quick connect "T" fitting equipped with a septum port on one of the ends to connect the probe to the vacuum system (see Figure 2-5),

- modeling clay,
- vacuum device or pump to create a flow of 100cc per minute (see Figure 2-5),
- 1/4 inch teflon tubing to go from the "T" fitting to the vacuum or pump (see Fig. 2-5),
- metal detector or magnetometer for detecting underground utilities/pipes/drums,
- two 100 $\mu$ l syringes for sampling,
- adjustable wrench for assembling sampling system, and
- teflon tape to seal joints on sampling system.

## **2.5. REAGENTS**

The following reagents are required:

- deionized, organic - free water for decontamination
- methanol for decontamination

## **2.6. PROCEDURES**

### **2.6.1. Soil Sampling Grid**

Using a map of the area, set up a soil sampling grid. Ensure enough samples are taken so that contamination will not likely be missed and that if contamination does exist, a plume can be mapped. This requires judgment of the analyst.

### **2.6.2. Soil Gas Sample Hole Installation**

The procedure consists of the following steps:

1. Drive a hole slightly deeper than the desired depth. For sampling at 4 feet, use a 5 foot extension for the slam bar and drive to approximately 4.5 feet. For deeper depths, use additional threaded extensions for the slam bar.
2. After the hole is made, carefully withdraw the slam bar extension to prevent collapse of the walls of the hole. Insert the soil gas probe.

3. Set probe to desired depth of sample and clear with wire or cable. Remove cable prior to sampling. Seal the top of the hole around the probe with modeling clay.

### **2.6.3. Screening with Field Instruments**

The procedure consists of the following steps:

1. The sampling hole volume must be evacuated prior to sampling. Connect the vacuum pump and evacuate the probe for approximately 10 seconds at 300 cc/min. for a 4.5 foot hole. More time is required for deeper holes. Allow the soil gas to equilibrate approximately 3 to 5 minutes before proceeding.
2. After evacuation, adjust the flow to 100 cc/min. and take samples with a 90  $\mu$ l sample with a syringe for analysis (a 90  $\mu$ l sample is taken as syringes tend to disperse less accurately at below 10 and above 90 % of capacity).

## **2.7. QUALITY CONTROL/QUALITY ASSURANCE**

Ensure sample probe is decontaminated after each well sampling by drawing ambient air through the probe and sampling the probe. If readings are higher than background air, further decontamination of the probe by washing with deionized, organic - free water and methanol is required. Having additional probes on hand is desirable so the analyst will not have to be decontaminate immediately.

### **3. RESULTS**

#### **3.1. CALCULATIONS**

The Photovac 10Splus calculates both the area of the peak and provides the concentration of the target compounds. However, both cannot be displayed at the same time on the chromatogram. Only concentrations are presented in this project. Concentration calculations are computed in the same way as the sample calculation in Appendix B (Sample Calculations and Calibration).

#### **3.2. NOTES**

The results are displayed separately for each area of campus that was surveyed. Each area begins with a map of that area followed by a table that presents a part per billion concentration of each compound tested. The alpha numeric designation for each analysis result site is displayed on the map in its approximate location. Detailed chromatograms for each analysis are presented in Appendices C through F. The alpha numeric designation for each sample location is in the notes section in the lower right hand corner of each chromatogram.

#### **3.3. MANUAL INTEGRATION**

The computer did not recognize all of the peaks on some of the analyses in some instances. When these peaks were of relatively significant size (10 ppb or greater), the peaks were manually integrated using the Chromatographer program (Photovac 10S COMM+ PC Software). These manual integrations can be identified by a small "a" following the alpha numeric designation.

### 3.4. SIGNIFICANCE OF FINDINGS

#### 3.4.1. State of Indiana Standards

The State of Indiana produces cleanup goals for specific substances in groundwater. No specific goals were found for soil. The following is a list of groundwater cleanup goals for the compounds tested in this survey [15]:

- Benzene -- 98.6 $\mu$ g/L,
- Trichloroethylene -- 260.0 $\mu$ g/L,
- Toluene -- 20440.0 $\mu$ g/L,
- Tetrachloroethylene -- 56.1 $\mu$ g/L,
- Ethylbenzene -- 10220.0 $\mu$ g/L, and
- Xylenes -- 204400.0 $\mu$ g/L.

None of the samples produced results exceeding the cleanup goals, though the following example of Benzene (Chemical Storage Building I) was the closest. Since the concentration of a substance in liquid (water) is the concentration in gas (air) divided by Henry's law constant,

$$\text{or } C_L = C_A / H$$

where  $C_A = 391.10 \text{ ppb}$ , and  $H = 71 \text{ ppb} \cdot \text{L}/\mu\text{g}$  [9: 741]

$$C_L = 5.508 \text{ } \mu\text{g/L}$$

The sample is 1.44 orders of magnitude less than the standard of 98.6  $\mu$ g/L.

#### 3.4.2. Background Concentrations

Background (ambient) air is the air above ground that is sampled prior to running the day's in ground samples. These analyses can be compared to the in ground analyses to further define the source of contamination. These had little value in this project as the samples were collected at a depth that should be unaffected by ambient conditions. In most cases the ambient concentrations were lower than the sample concentrations, however, this was not always the case. Most likely bacterial microdegradation of organic material in the top layer of soil (top 2

feet) was responsible for negating the possible effects of adsorption and transport of ambient contaminants. This would hold true unless ambient concentrations were extremely high, which they were not when tested.

### 3.4.3. Contamination Tracking

No tests were conducted of the area groundwater. However, by determining maximum solubility of each substance in water at ambient temperature, and determining the corresponding concentration of substance in the soil gas over the groundwater, some conclusions can be drawn. As an example, the vapor pressure of benzene at 10°C (approximate soil temperature at 4ft) is determined by the Antoine Equation (see Appendix A), or

$$\log P = 6.01905 - [1204.637/(10^\circ\text{C} + 220.069)]$$

so:

$$P = 6.068\text{kPa} = 0.060\text{atm}$$

and since

$$\text{Solubility (S)} = P/\text{Henry's constant (H)},$$

$$S = 0.060 \text{ atm}/5.53 \text{ atm} \cdot \text{m}^3/\text{mol} = 0.0109 \text{ mol/m}^3 = 1.086 \times 10^{-5} \text{ mol/L}.$$

Multiplying by the molecular weight of  $78.11 \times 10^3 \text{ mg/mol}$ , the maximum concentration is  $0.8485 \text{ mg/L} = 848.5 \mu\text{g/L}$ , which multiplied by Henry's constant for Benzene (71 ppb • L/μg) produces a concentration over the dissolved Benzene of:

$$60243.5 \text{ ppb} = \mathbf{60.2435\text{ppm}}.$$

The maximum concentration of benzene in air occurs over the pure solvent where:

$$C \text{ ppm} = (P/101.325 \text{ kPa})(1 \times 10^6) = \mathbf{59886.504\text{ppm}}.$$

Therefore, concentrations less than 60.2435ppm (as in all samples in this project) might come from the groundwater, solvent, or both. Also, concentrations greater than 60.2435 must come at least partially from solvent.

More information may be obtained about the specific conditions at a testing site by sampling and analyzing the groundwater and soil. Photovac has produced two documents that

outline procedures for attaining this information. "Procedure for Preparing Soil and Water Samples for Analysis by Portable Gas Chromatograph", Photovac TechTips Volume 2, Number 3, March 1996, outlines a procedure to sample soil and water samples. "Monitoring Trace Levels of Trichloroethylene and Tetrachloroethylene in Water Using the 10S Plus Portable Gas Chromatograph", Photovac TechTips Volume 2, Number 4, March 1996, outlines a procedure to analyze trace contaminants in the headspace above a water sample.

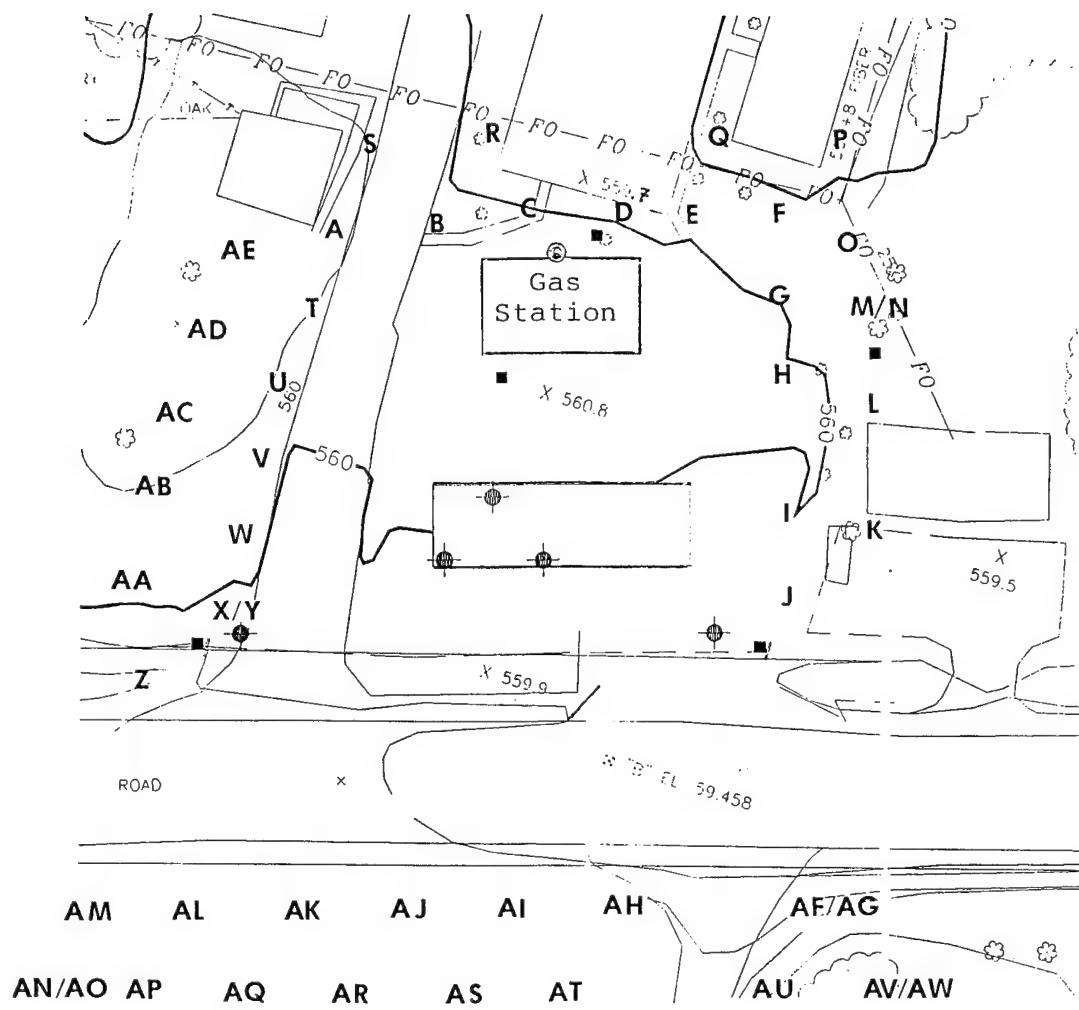


Figure 3-1

**Gas Station Map**

Table 3-1

## Gas Station Results (ppb)

Analysis	Benzene	Trichloroethylene	Toluene	Tetrachloroethylene	Ethylbenzene	m & p xylene	o xylene
A	107.70	19.35	33.51	0.00	153.00	125.20	61.00
B	121.40	18.06	31.01	0.00	133.10	97.88	50.11
C	100.30	15.28	42.81	0.00	145.00	72.54	0.00
D	29.69	4.32	14.01	11.06	136.60	0.00	0.00
E	43.22	7.14	17.03	3.76	164.70	25.79	0.00
F	36.51	6.77	15.70	4.84	156.80	23.58	0.00
G	33.91	7.27	37.52	9.26	180.60	36.64	0.00
H	35.66	6.57	168.20	3.43	174.00	28.07	0.00
I	43.73	10.40	94.26	3.52	178.80	43.34	0.00
J	30.48	6.31	12.06	2.73	185.40	26.66	0.00
K	49.58	11.14	19.17	3.74	175.60	36.67	0.00
L	48.74	9.64	14.58	3.89	155.60	31.12	0.00
M	44.98	12.10	17.24	0.00	165.00	24.98	0.00
N	41.47	12.97	26.32	2.65	157.00	25.46	0.00
O	45.15	15.28	23.97	7.12	123.30	22.14	0.00
P	37.44	14.29	24.76	3.85	120.80	0.00	0.00
Q	40.06	12.66	41.74	3.36	127.80	0.00	0.00
R & Ra	29.29	9.38	32.96	3.60	160.60	32.05	0.00
S	46.99	15.50	46.98	3.04	136.40	14.96	0.00
T	32.91	12.06	23.16	3.38	184.10	37.38	0.00
U	34.11	10.70	16.89	3.81	155.00	0.00	0.00
V & Va	22.43	8.40	25.68	13.12	147.30	0.00	0.00
W	27.76	12.72	22.10	2.64	174.60	40.70	0.00
X	0.00	0.00	18.56	7.59	135.40	68.17	0.00
Y	0.00	0.00	12.09	9.86	164.00	79.20	0.00
Z	0.00	0.00	48.67	10.75	158.80	110.00	32.12

Table 3-1 continued

## Gas Station Results (ppb)

Analysis	Benzene	Trichloroethylene	Toluene	Tetrachloroethylene	Ethylbenzene	m & p xylene	o xylene
AA	0.00	0.00	0.00	7.53	137.80	80.52	19.88
AB	0.00	0.00	17.10	8.36	155.20	111.40	0.00
AC	0.00	0.00	34.05	9.30	182.00	92.61	23.22
AD	0.00	0.00	0.00	10.36	201.10	107.90	27.53
AE	0.00	0.00	7.13	8.91	188.50	111.00	31.03
AF	82.26	0.00	8.38	9.14	142.80	54.05	21.94
AG	68.72	0.26	12.79	9.64	198.50	127.10	49.96
AH & AH <sub>a</sub>	53.35	1.69	9.49	7.09	163.20	83.23	96.78
AI	70.43	23.49	94.94	31.61	272.80	160.20	74.04
AJ & AJ <sub>a</sub>	50.30	2.24	13.71	9.48	224.80	170.60	76.71
AK & AK <sub>a</sub>	60.81	2.56	16.65	9.70	205.60	103.30	35.59
AL & AL <sub>a</sub>	18.27	9.95	7.62	2.24	181.40	42.77	28.96
AM	189.10	3.92	31.93	21.74	162.60	238.70	74.46
AN & AN <sub>a</sub>	74.40	2.37	25.77	17.27	191.30	233.00	78.28
AO & AO <sub>a</sub>	78.65	2.95	68.16	16.54	207.80	212.10	74.67
AP	59.80	1.49	17.63	15.34	219.50	198.90	58.57
AQ & AQ <sub>a</sub>	37.51	1.68	55.95	11.18	338.90	162.40	62.84
AR & AR <sub>a</sub>	47.70	1.73	21.87	14.50	247.30	170.80	128.50
AS	74.58	1.99	23.71	19.52	283.70	253.70	87.69
AT & AT <sub>a</sub>	38.85	1.61	102.80	12.34	335.80	164.50	56.58
AU	75.78	1.98	37.33	16.67	279.20	221.60	70.52
AV & AV <sub>a</sub>	57.69	2.05	26.87	14.40	249.30	175.00	47.01
AW & AW <sub>a</sub>	47.90	1.84	94.29	13.51	259.10	205.70	55.17

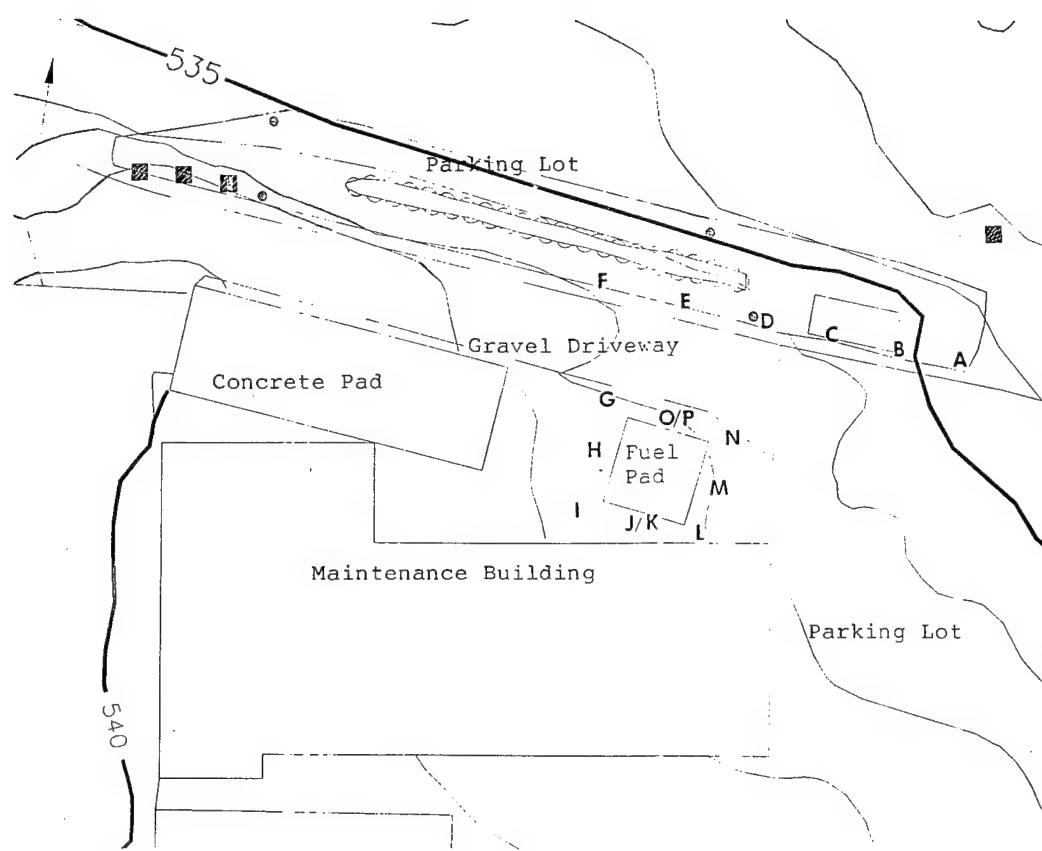


Figure 3-2  
Maintenance Operation Map

Table 3-2

## Maintenance Operation Results (ppb)

Analysis	Benzene	Trichloroethylene	Toluene	Tetrachloroethylene	Ethylbenzene	m & p xylene	o xylene
A	146.50	0.00	10.35	12.81	198.80	164.60	51.89
B & Ba	121.50	0.00	18.17	12.86	187.90	153.60	48.49
C	191.90	1.34	31.46	17.60	255.10	207.70	66.49
D & Da	107.80	1.30	11.70	13.18	225.80	157.80	55.67
E & Ea	111.20	1.05	8.24	10.20	238.10	155.60	47.20
F	134.90	21.10	43.61	18.72	265.70	137.60	40.40
G & Ga	103.00	2.80	0.00	15.65	249.80	153.10	44.72
H	80.34	0.00	13.14	9.91	229.10	105.00	0.00
I	109.90	13.98	24.93	15.49	250.70	103.30	58.16
J	174.10	186.10	393.50	66.60	911.80	358.30	143.60
K	183.70	53.05	239.30	26.31	352.30	264.50	108.30
L & La	111.50	2.73	44.93	15.02	291.70	165.30	53.52
M	113.40	2.08	7.11	14.01	295.20	134.70	42.91
N & Na	82.30	1.49	17.39	12.95	268.00	176.80	45.92
O & Oa	91.68	0.97	6.93	28.68	248.20	148.90	45.39
P	64.82	0.48	0.51	28.43	220.20	104.80	27.90

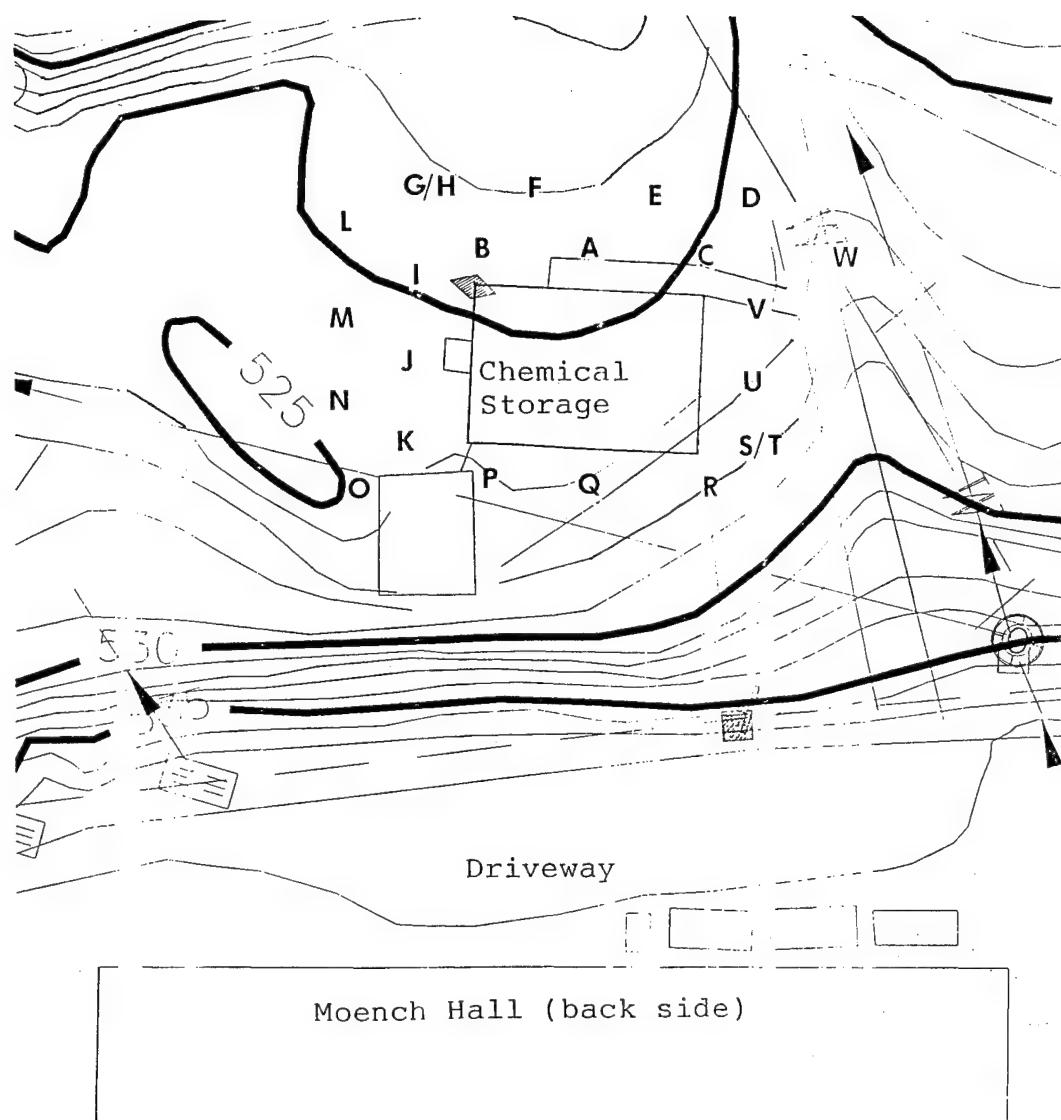


Figure 3-3

**Chemical Storage Building Map**

Chemical Storage Building Results (ppb)

Table 3-3

Analysis	Benzene	Trichloroethylene	Toluene	Tetrachloroethylene	Ethylbenzene	m & p xylene	o xylene
A	37.63	9.99	182.20	78.23	124.40	662.80	237.40
B	0.00	18.07	517.80	47.93	91.89	443.30	153.00
C	0.00	39.33	54.38	50.57	84.13	452.80	127.60
D	0.00	14.54	98.09	51.36	76.00	425.40	136.80
E	0.00	9.17	13.06	52.41	47.00	433.50	125.90
F	0.00	5.06	168.30	28.77	41.72	235.10	70.59
G	0.00	6.16	36.19	39.15	46.00	295.00	77.09
H	0.00	6.22	67.18	41.44	42.67	318.60	90.09
I	391.10	38.02	59.54	0.00	42.43	158.30	55.28
J	59.97	5.74	67.64	18.48	112.30	172.70	49.73
K	13.60	0.00	0.00	5.35	177.30	45.67	0.00
L & La	7.72	15.41	11.21	3.51	155.40	0.00	0.00
M	30.71	0.64	16.52	10.62	174.70	119.80	17.67
N	52.56	0.30	21.51	13.21	190.40	120.50	25.27
O & Oa	9.94	14.94	0.00	0.00	138.50	0.00	0.00
P & Pa	17.21	1.17	12.11	8.15	193.80	81.00	0.00
Q	7.81	0.00	0.00	2.88	172.10	24.51	0.00
R	0.00	0.00	0.00	5.21	184.10	34.76	0.00
S & Sa	14.89	0.00	0.00	7.89	184.90	73.63	0.00
T & Ta	16.15	0.00	6.23	9.01	201.80	89.91	0.00
U & Ua	13.42	0.00	45.95	7.66	211.50	78.85	0.00
V & Va	13.87	0.00	0.00	7.63	193.60	81.88	0.00
W & Wa	21.41	16.70	9.96	16.70	187.50	80.05	0.00

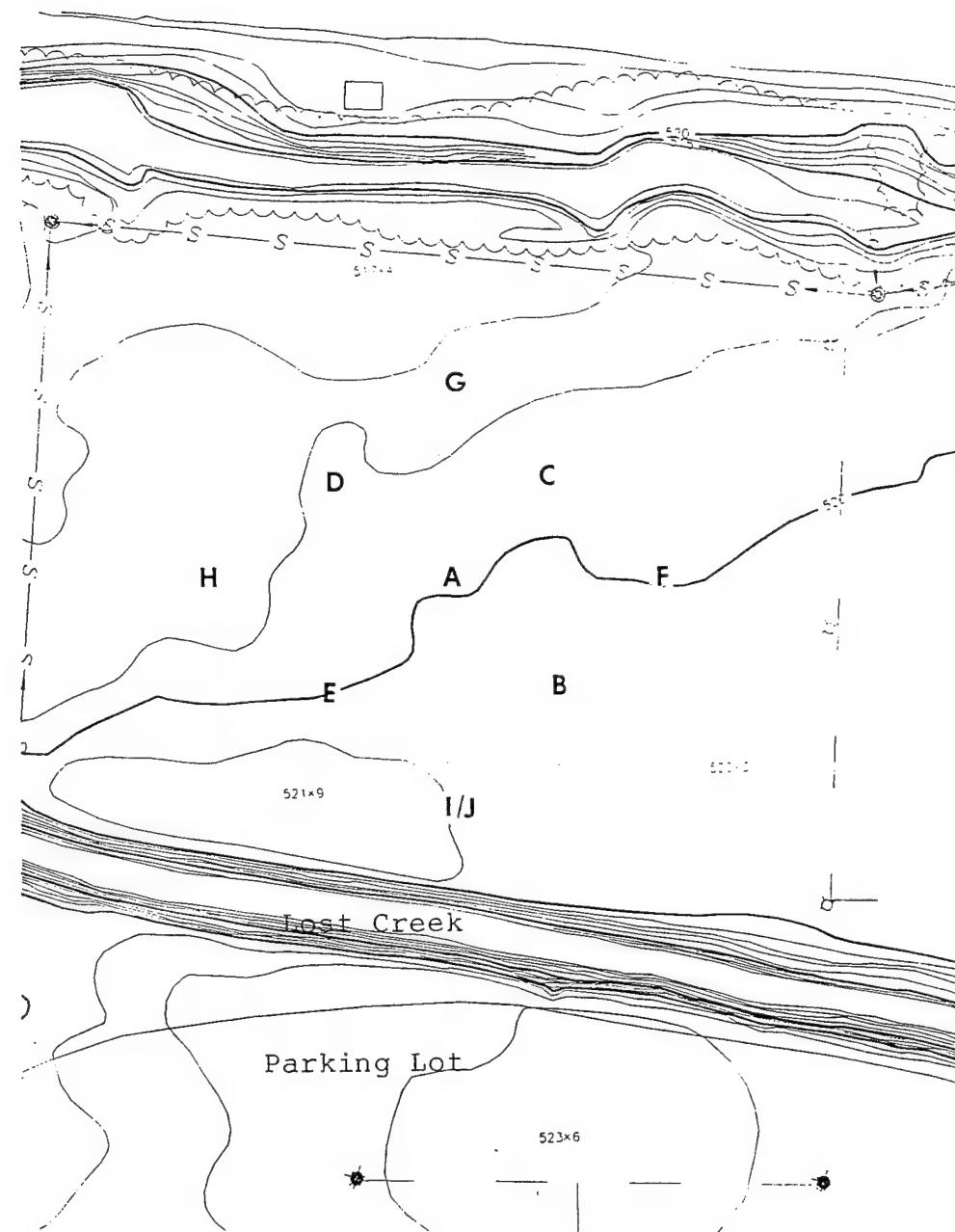


Figure 3-4

**Bonfire Site Map**

Table 3-4

## Bonfire Site Results (ppb)

Analysis	Benzene	Trichloroethylene	Toluene	Tetrachloroethylene	Ethylbenzene	m & p xylene	o xylene
A	0.00	5.59	12.56	0.00	108.30	7.71	0.00
B	0.00	0.00	7.63	0.00	125.00	0.00	0.00
C	1.59	0.00	7.99	0.00	166.30	0.00	0.00
D	0.00	2.69	13.10	2.98	158.20	0.00	610.40
E	18.93	0.00	15.72	3.23	145.10	0.00	0.00
F & Fa	11.10	3.49	15.17	4.49	155.50	0.00	0.00
G	9.31	3.40	14.49	3.72	151.20	0.00	0.00
H & Ha	11.00	2.96	10.35	0.00	146.90	0.00	0.00
I	0.00	0.00	10.28	0.00	141.70	0.00	0.00
J	0.00	0.00	9.89	0.00	188.00	0.00	0.00

## 4. REMEDIATION

Though no significant contamination was found on the Rose-Hulman property, a short discussion of liability and remediation will still be presented.

### 4.1. LIABILITY

According to the CERCLA, basically anyone may be held liable who had anything to do with a contaminated site. These potentially *responsible parties* (RPs) may be the historic owners or operators of the site, any generators who disposed of wastes at the site (whether legally or not), the transporters who brought the wastes to the site, or any combination of the above. The courts have also upheld the concept of *joint and several liability*, which means, in essence, that if damages cannot be individually apportioned by the responsible parties themselves, then each and every party is subject to liability for the entire cleanup cost. So no matter how little a single RP may have contributed to the overall problem, he may be held liable for the entire cleanup. Further, if the RPs do not voluntarily cleanup the site the Environmental Protection Agency can use Superfund monies to conduct the cleanup and charge the RPs up to three times the cost of the cleanup [14: 190].

The recovery of cleanup costs may also be accompanied by criminal cases. Though much more rare, these cases have sent individuals to jail when laws were inadvertently broken or intentionally ignored.

#### **4.2. REMEDIATION OPTIONS**

Numerous options are available to remediate sites. These include high temperature incineration, hazardous waste landfill disposal, vitrification (intense heat to solidify the waste making it less mobile), solvent extraction (using a solvent to separate hazards from soil), and soil stripping (pumping air into a closed soil system and capturing the air with volatile organics on the other end). Additionally, a great deal of research is being conducted to create new remediation technologies, reduce the cost of existing technologies, and improve the efficiency of existing technologies.

The best course of action, however, is to not create the situation in the first place. By reducing the use of hazardous materials, reusing hazardous materials until they are no longer useful, and recycling materials once they are no longer useful in their current form, remediation can be avoided.

## 5. CONCLUSIONS AND RECOMMENDATIONS

### 5.1. CONCLUSIONS

The Rose-Hulman Institute of Technology campus does not appear to have any major areas of contamination of the most common volatile organic compounds found at hazardous waste sites. There are, however, three sites of concern: (1) the maintenance operation area; (2) the chemical storage building; and (3) the underground heating oil tank for the student union building.

The maintenance operation area uses solvents, paints, and fuels in its day to day operations. The disposal of excess materials and the handling of hazardous materials is a constant concern not only for the health of the employees, but also for liability purposes.

The chemical storage building is a concern in that several old and rusty 55 gallon drums of unknown material are being stored in the facility. Though the building is vented through the roof, a strong odor of chemicals is present in the air. Further, no system to trap liquid leaks exists.

The underground heating oil tank is a concern because of the possibility of leakage to Lost Creek which is within 50 meters of the tank. No tests were conducted near the tank due to temporary electrical service wires being used for the construction on the student union expansion project.

## **5.2. RECOMMENDATIONS**

### **5.2.1. Maintenance Operation**

The maintenance operation should develop and execute standard operating procedures (SOPs) with regard to hazardous waste. The RCRA, the Uniform Building Code, and the local fire code provide standards in this area. At a minimum these SOPs should include:

- a list of all substances used by the operation that contain hazardous substances,
- the proper disposal method for these substances,
- the proper handling of these substances,
- the proper storage of these substances,
- accurate inventory and control of the substances, and
- periodic inspections conducted by management to ensure compliance with the SOPs.

### **5.2.2. Chemical Storage Building**

The 55 gallon drums of unknown substances in the chemical storage building should be disposed of in accordance with EPA guidelines established by the RCRA. In addition, a system to trap potential spills of liquid hazardous substances should be installed. Finally, periodic gas chromatograph monitoring of the air in and around the structure would be prudent in order to avoid health risk to users of the facility. Because a large number of compounds are present in the chemical storage building, standards containing most, if not all, of these compounds should be purchased commercially. Substances that need to be tested for that are not available in a commercial standard, may be added to the library using the method described within this research.

### **5.2.3. Institution Policy and Procedure**

The institution should develop a policy for all departments dealing with hazardous materials, to create an SOP similar to the one suggested for the maintenance operation. Additionally, yearly monitoring of all the sites included in this research and the heating oil underground storage tank would be wise. An inexpensive way to conduct this monitoring would be to have students develop and execute a faculty approved sampling/monitoring plan. A project like this might be developed and accomplished as a group senior project or by a graduate student.

### **5.2.4. Analysis Limitations**

Since not all possible contaminants were tested for in this project, additional testing of other contaminants such as additional volatile organics and/or pesticides might be prudent.

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## REFERENCES

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## APPENDIX A

### PHOTOVAC 10Splus PORTABLE GAS CHROMATOGRAPHY PROCEDURES

U.S. Environmental Protection Agency Standard Operating Procedures #2108, #2109 and the Photovac 10Splus User's Manual were used as the base documents for this procedure.

#### 1. EQUIPMENT DESCRIPTION AND METHOD SUMMARY

The Photovac 10Splus is a battery operated/AC operated, portable gas chromatograph with a photoionization detector (see Figure A-1). It is a field/laboratory instrument capable of screening for many organic vapors using an ultraviolet light source and photoionization detector. The compounds are ionized with ultraviolet light as they emerge from the column. The ions are then attracted to an oppositely charged electrode which causes a voltage in mV. Gaseous contaminants are identified by comparing retention times in the column with previously identified substances. The voltage is multiplied by the time required for the peak to subside in the internal microprocessor to determine concentration as a relative area in mVs to previously calibrated concentrations to determine sample concentration.

#### 2. INTERFERENCES AND POTENTIAL PROBLEMS

##### 2.1. Temperature and Humidity

The Photovac 10Splus portable gas chromatograph must be operated within the appropriate temperature and humidity tolerances. The operating temperature should be between 10 and 40°C and the humidity between 0 and 95% (non-condensing) [3: 205].

Though the instrument contains an internal temperature - controlled oven, Photovac suggests that it is best used in stable, temperature - controlled environment to avoid fluctuating retention times which may occur with changing temperatures.

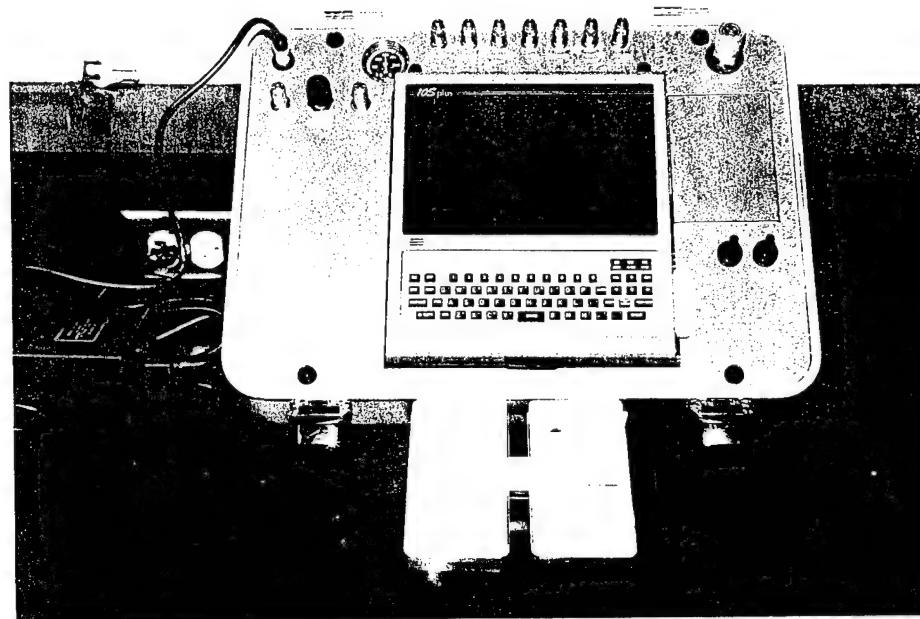


Figure A-1

**Photovac 10Splus**

## **2.2. Compound Misidentification**

Target compounds in gas chromatography are identified by their retention times (Rts). If the retention time of the sample matches the retention time of the standard, they are assumed to be identical. Therefore, a compound with a similar retention time as the standard may be misidentified as the target compound.

### **3. EQUIPMENT/APPARATUS**

#### **3.1. Equipment List**

The following is a list of required equipment:

- Photovac 10Splus GC with user's manual and power cord (see Figure A-1),
- zero air carrier gas,
- septa, 6mm diameter,
- Snoop leak detection compound (used on gas fittings within gas chromatograph to identify leaks),
- lint/static free wipes to clean LED display on gas chromatograph,
- High Pressure Filling Station (see Figure A-2),
- Photovac Air Flow Meter (see Figure A-3),
- one liter glass septum bulbs (see Figure A-4),
- 40ml septum - topped vials (see Figure A-4), and
- syringes, gas tight (see Figure A-4).

#### **3.2. Carrier Gas**

Zero compressed air is used. Ultra zero may be used for applications requiring < 0.1 ppm total hydrocarbon content.

### **4. PROCEDURES**

#### **4.1. Carrier Gas Filling Procedure**

The Photovac contains an internal reservoir for the carrier gas supply. To recharge the reservoir, the High Pressure Filling Station is required. This device consists of the high pressure connection for cylinder attachment followed by a two - way valve (see Figure A-2). The two - way valve can be positioned to deliver gas from the cylinder to a long flexible hose and then to

the refill receptacle located on the top right on the control panel (see Figure A-1). A pressure relief valve is provided for safety at the upper end of the flexible hose. This is set at 1700 psi. A flow restricter is also incorporated in line with the hose, to limit the escape rate of gas. **Under no circumstances should the high pressure filling station be modified or disassembled by the user.** In the event of problems, the unit must be returned to Photovac for repair or replacement. The procedure is as follows:

1. Attach the high pressure fitting to the gas cylinder and turn the valve handle so it points away from the cylinder.
2. Open the cylinder valve and check for leaks.
3. Now turn the filling station valve so that it points toward the cylinder. A steady flow of gas will be heard escaping from the end of the flexible hose; this purges the hose of any impurities.

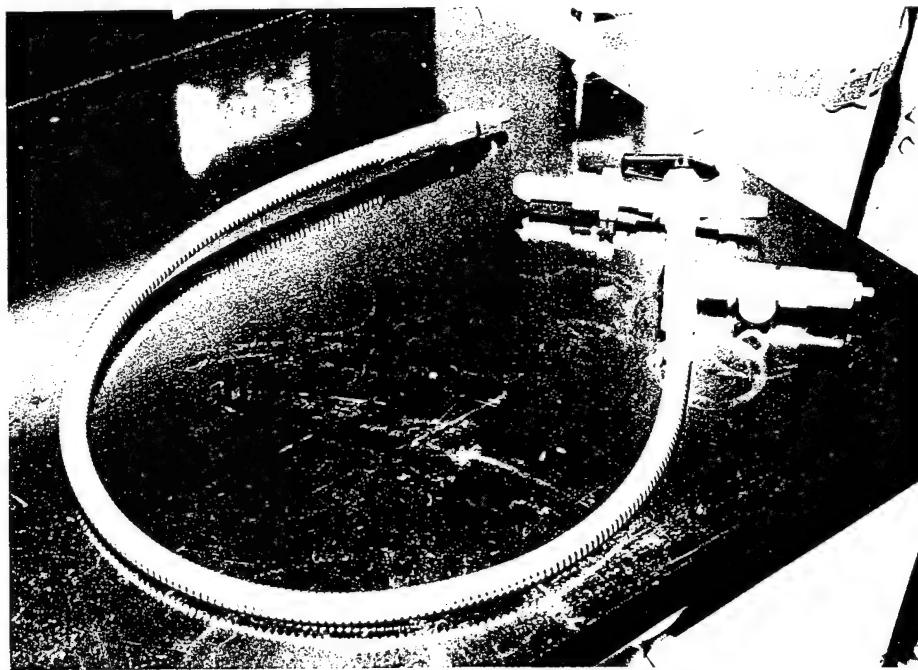


Figure A-2

Photovac High Pressure Filling Station

4. Return the filling station valve to its previous position (closed).
5. Place the Photovac on a sturdy, flat surface within easy reach of the flexible receptacle. Press in firmly until a click is heard (locked on position).
6. Turn the filling station valve until it again points toward the cylinder and carefully watch the contents gauge on the upper left hand portion of the control panel on the GC.
7. As the needle reaches 1600 psi, the pressure relief valve on the high pressure filling station should prevent further increase. The pressure indicated on the contents gauge must not exceed 1800 psi; switch off the pressure manually if the pressure relief valve fails to govern this. Close the valve on the gas cylinder. Switch the high pressure relief valve after filling to release excess pressure in the hose prior to removal. A check valve in the GC will keep the carrier gas from leaking out of the system.
8. Remove and store the filling station so that does not become damaged.

#### **4.1.1. Reagents**

The following reagents are required:

- carrier gas, zero air
- appropriate calibration standards

#### **4.2. Operating Procedures**

##### **4.2.1. Pre - Operational Checks**

The following checks are required:

1. Check the instrument for any obvious damage. Plug the power cord into an AC power source, if available.

2. Raise the computer module. Check that all compression fittings associated with the column and all valves which are subject to carrier gas flow are finger tight. **Do not overtighten.** Fittings may loosen in transit. Check which injection port is connected to the columns (only one may be connected at a time). Close the computer module.

3. Check that the 6mm septum is new on the injection port. Make sure that the septum retainer/needle guide is tight. **Do not overtighten.**

4. Ensure carrier gas flow is engaged by ensuring tank is pressurized (flow exists when tank is pressurized).

#### 4.2.2. Start -up and Carrier Gas Flow Rate Adjustment

Adjust the flow rate as follows:

1. Remove the fittings from the BKFLUSH OUT, CAL IN, SAMPLE IN, DET OUT, and PUMP OUT ports.

2. Turn on the machine.

3. Place card #2 in the machine so the system can self load (complete when green card light begins flashing). Remove card #2.

4. Place card #1 into the machine. Highlight the GC.bin file. Press the COMMAND key and move the cursor to File and press ENTER. Select Run, confirm the GC.bin file, move the cursor to OK, and press ENTER. When the card light flashes, remove card #1.

5. Place the data card in the machine. Press the FCN button. Press the COMMAND button and select File and press ENTER. Select the file to be used or create a new method, move the cursor to OK and press ENTER.

6. Set carrier gas flow rate by attaching the bubble flow rate (see Figure A-3) indicator to the DET OUT port and adjusting the CARRIER CONTROL VALVE so the flow rate is 10.0 mL/min for capillary columns.

7. Disconnect the flowmeter from the DET OUT port.

8. To balance the flow rate with the GC method, open the method menu. Check the flow rates entered and adjust the flow rate of the DET OUT port and the BKFLUSH OUT port to those values. This is done by attaching the flowmeter to the BKFLUSH OUT port and adjusting the BKFLUSH CONTROL valve until 10.0 mL/min is reached. Reconnect the flowmeter to the DET OUT port and recheck the flow rate. About 20 seconds is needed between connections to stabilize flow. Once stabilized, they may both be adjusted by using the CARRIER CONTROL valve.

9. After flow rate through the detector is set, turn on the instrument by going into the analyzer menu, opening the status dialog box, and entering GC Detector On.

10. The lamp status will change to Tuning. When the UV lamp has tuned, the lamp status will change to Started OK or On and Reset and you will hear a beep. Allow an additional 20 - 30 minutes for the oven to heat up and stabilize.

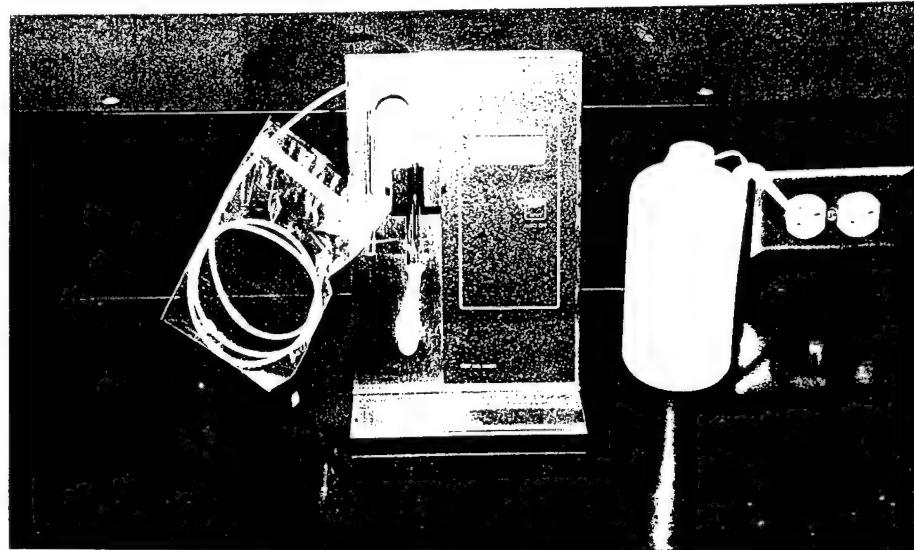


Figure A-3

**Photovac Air Flow Meter**

11. For at least one hour prior to use, purge the instrument (column, valve, detectors) of residual contamination encountered in transit by carrier gas flow (simply leave the instrument on). Overnight decontamination may be necessary.

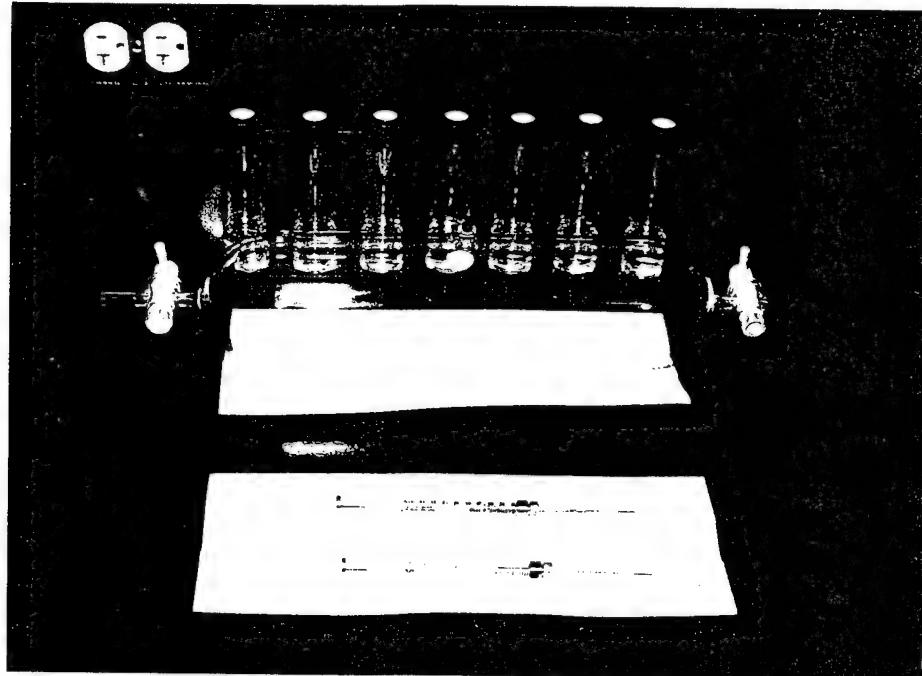


Figure A-4

#### **Glassware and Syringes**

##### **4.2.4. Datalogging Options**

Results may be logged to a RAM card or directly to a printer using the Log menu. In this case all analysis was logged to a RAM card then to the 10S COMM + PC Software (see Figure A-5). Table A-1 contains a list of extensions for specific types of data.

The only option used in this survey was the RAM card option, so it is the only one discussed in detail. The process is as follows:

1. Open the Log menu and select Avg/Max.

2. In the Avg/Max dialog box enter the start and stop time for each period. You do not need to use all four periods if you do not need them. Ensure that the periods you use cover the duration of your monitoring. If the period times overlap, a warning message will be displayed. If no period is entered, data will be logged for a 24 hour period.

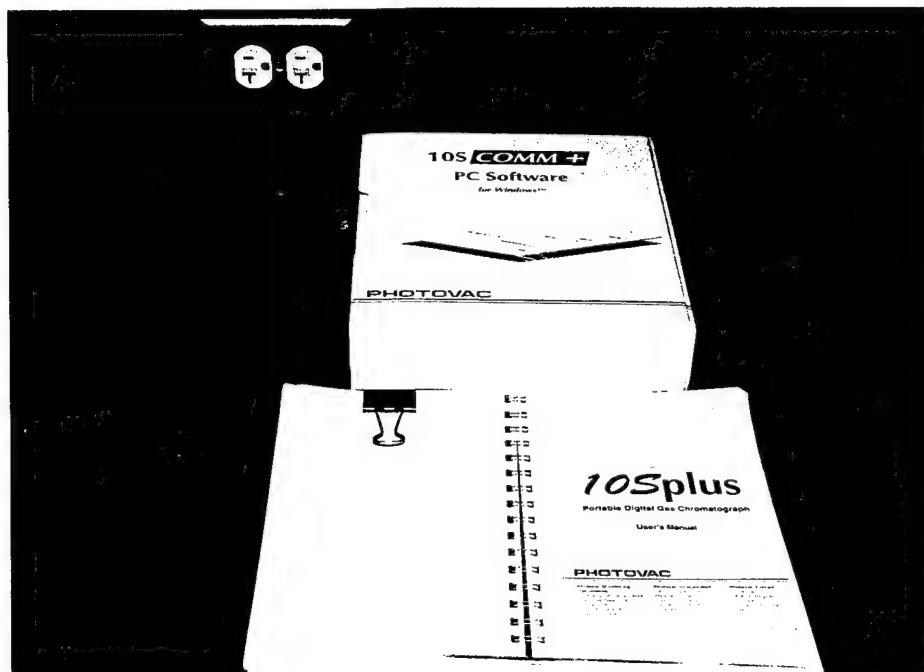


Figure P-5

#### 10S Comm + PC Software

3. Open the Log menu and select RAM disk.
4. Monitor the screen to see if any changes need to be made to the method.

Select the file types that you want to log and name the files per Table A-2.

5. If the card becomes full, use a new card or erase old files to make room for the new ones.
6. Select whether you want undetected compounds entered in the log files as 0 ppm or omitted from the log file altogether.

7. Press exit to close the dialog box.

Table A-1  
**File Name Formats**

EXTENSION	TYPE OF DATA COLLECTED
.gc	Chromatogram
.an	All analysis including calibration, alarms, and faults
.al	Analysis with alarms only
.cl	Calibrations only
.fl	Analysis with faults only
.av1	Avg/Max report for the first period
.av2	Avg/Max report for the second period
.av3	Avg/Max report for the third period
.av4	Avg/Max report for the fourth period

Table A-2  
**File Name Formats**

File Name = YYMMDDXX.EXT	
YY	Year
MM	Month (JA, FE, MR, AP, MY, JN, JL, AU, SE, OC, NV, and DE)
DD	Day
XX	Unique identification code for GC files only, as there will be more than one per day.
.EXT	See Table P-1 for appropriate file extension.

#### 4.2.3. Performing a Syringe Injection Analysis

The following steps are taken to perform a syringe injection analysis:

1. Install the sample loop purge tube between the BKFLUSH OUT and SAMPLE IN ports.

2. Open the method menu and move the cursor to Syringe and press ENTER.

A check mark will appear beside the option.

3. Flush a 100  $\mu\text{L}$  syringe with sample and then draw a 90  $\mu\text{L}$  sample. Have the syringe sample ready before pressing RUN AUTO.

4. Guide the syringe needle through the hole in injection port 1 until the needle touches the septum, but do not pierce the septum or depress the plunger yet.

5. Press RUN AUTO or select Start Analysis in the Analyzer menu. Select and enter Sample from the window that opens. After the buzzer sounds, push the needle through the septum until the barrel comes up against the injection port and immediately depress the plunger with a smooth, rapid motion.

6. Leave the syringe in place for about 2 seconds then withdraw it.

Note: if you are using syringe injection to analyze samples, you must calibrate using syringe injection.

7. The chromatogram will now begin to develop on the screen.

#### **4.2.5. Standards and Calibration Procedures**

The standards used in this survey were developed from volatile liquid headspace. **Always observe proper handling procedures when dealing with these solvents to include the use of a fume hood.**

##### **4.2.5.1. Standards Preparation**

Standards are prepared as follows:

1. Fill a glass two - way, septum port equipped, gas sampling bulb (see Figure A-4) with zero air. This is accomplished by:

A. closing the septum on the bulb and opening both stop cocks,

- B. attaching a high pressure tank of zero air to one end of the bulb,
- C. carefully opening the valve on the tank to allow air to pass through the bulb (care should be taken to not overpressurize the bulb so it doesn't shatter; and safety glasses should be worn),
- D. after the bulb has been flushed (5 seconds or longer depending on the amount of contamination), close the bulb on the gas inlet side and then immediately close the gas outlet side. The bulb is now ready to accept the volatile liquid headspace.

2. In a fume hood fill a 40mL septum topped screw cap vial approximately one quarter full of pure solvent. Cap the vial.
3. Repeat this procedure for each solvent to be used.
4. Use the following equations for each solvent to determine the volume of headspace required for a target ppm concentration in one liter of air (repeat the calculation for each solvent to be tested): [13: 1-2]

**Antoine Equation**

$$\log P^\circ = A - B / (t + C)$$

where:

$P^\circ$  = vapor pressure (kPa);

$t$  = temperature ( $^{\circ}\text{C}$ ); and

$A$ ,  $B$ ,  $C$  are constants characteristic of the compound (see Table A-3)

and

$$V_h = (101.325 \text{ kPa} / P^\circ \text{ ambient}) (C_{\text{ppm}}) (V_L)$$

where:

$V_h$  = volume (microliters) of saturated headspace

$C_{\text{ppm}}$  = desired concentration (parts per million)

$V_L$  = volume (liters) of the static volume dilution container

5. In a quick, smooth motion, inject the headspace from a single volatile liquid into the bulb and remove syringe. Allow a few seconds to equilibrate before use.

Table A-3  
Constants for the Antoine Equation [13: 3-4]

COMPOUND	A	B	C
Benzene	6.01905	1204.637	220.069
Ethylbenzene	6.08206	1425.305	213.415
Tetrachloroethylene	6.10343	1387.956	217.640
Toluene	6.37988	1575.007	249.372
Trichloroethylene	5.59553	994.460	189.705
o - xylene	6.12699	1476.753	213.911
m - xylene	6.13232	1460.805	214.895
p - xylene	6.11513	1453.812	215.420

Note: Alternately use Table A-4 to determine required volume of headspace.

Table A-4  
Headspace Volumes ( $\mu\text{L}$ ) for One Liter Standards at 1.0 ppm

COMPOUND	VOLUME	VOLUME	VOLUME	VOLUME	VOLUME	VOLUME
	AT 20° C	AT 21° C	AT 22° C	AT 23° C	AT 24° C	AT 25° C
Benzene	10.1	9.6	9.2	8.8	8.4	8.0
Ethylbenzene	107.1	100.9	95.0	89.6	84.5	79.8
Tetrachloroethylene	55.3	52.3	49.4	46.8	44.2	41.9
Toluene	29.7	28.2	26.9	25.6	24.4	23.2
Trichloroethylene	14.2	13.5	12.8	12.2	11.6	11.0
o - xylene	155.6	146.2	137.6	129.4	121.8	114.8
m - xylene	123.7	116.4	109.6	103.2	97.3	91.8
p - xylene	116.4	109.6	103.2	103.2	91.8	86.6

Adapted from: [13: 7, 11, 14-15]

Note: to make other concentration standards, adjust the volume of headspace linearly (as an example, a 10.0ppm standard requires ten times the headspace of a 1.0ppm standard).

#### 4.2.5.2. Building the Library

The Photovac 10Splus User's Manual is the primary reference for this section [3]. The procedure is as follows:

1. Set up the 10Splus for syringe injection. Ensure the sample loop purge tube is installed between the BKFLUSH OUT and the SAMPLE IN ports.

2. Withdraw the appropriate amount sample from the gas sampling bulb in accordance with the concentration and quantity figures you placed in the computer.

3. Press RUN AUTO and select Sample to run an analysis of the compound. Inject the sample as described in Section 4.2.3. (Performing a Syringe Injection Analysis).

If no peaks are stored in the library, then the peak will be listed as Unknown in the peak information. If peaks that are stored in the library match the retention times of the identified peaks, they will be identified the same. Compounds may also be identified as unknown if the oven temperature or flow rate has been changed as the compound will exit the column at a different time.

4. When the analysis is complete, open the Library dialog box in the Method menu.

5. Select and enter Store.

6. One of the positions beneath Name will be highlighted. If you are storing a compound that is already listed in the Library, move the cursor to that position and press ENTER. If you are storing a new compound, move the cursor to the first empty location on the compound list and press ENTER.

7. The Library Store dialog box will open. Enter the peak number from the results screen of the peak to be stored and press ENTER to confirm the number.

8. The cursor moves to the line where you enter the compound name (up to 16 characters). Enter Alarm 1 and Alarm 2 concentrations if necessary.

9. Each compound can be stored at up to three concentration levels for improved response linearity over the concentration range. Type in the concentration in the Conc 1 box and press enter. The measured peak area in millivolt - seconds will appear in the Response box beside the known concentration. After a few seconds the window closes. The compound has now been stored in the library.

10. Press EXIT to return to the Results screen.

11. Open the method menu and select and enter Re - integrate. The peaks in the Results screen will now be interpreted according to the integration method and the library information you just entered.

12. Repeat this procedure for all compounds to be tested in all three concentrations.

13. For unstable compounds you may conduct an average response by repeating steps one through eleven above, but in step five use Select average instead.

#### 4.2.5.3. Calibration

Calibration should occur after every eight hours of use or every day, whichever comes first. Calibration should also occur if the method has been altered [3: 65]. There are two basic forms of calibration: multi - component and surrogate. Multi - component calibration normally occurs when the analyst uses commercially prepared calibration gas containing all compounds of interest in known concentration levels. All compounds are adjusted in relation to the responses received for each compound during the analysis. Surrogate calibration is similar except only one known concentration gas is used. In this case, all compounds are adjusted as they relate to the calibrant compound. Surrogate calibration was used in this project and is accomplished by the following steps:

1. Open the Library dialog box in the Method Menu. In the Cal column, enter the concentration of the calibration compound. **Leave all other compounds as zero.**
2. Install the sample loop purge tube.
3. Open the method menu and ensure syringe is selected.

4. Prepare the syringe sample.
5. Press RUN AUTO and select Cal to run a calibration analysis. Inject the sample after the buzzer sounds. When the analysis is complete, the entire library will be updated.

## **5. QUALITY ASSURANCE/QUALITY CONTROL**

The following list should be followed and provided for the data package:

- Sample log to include the date/time of sample collection, the date/time of analysis, and information on the method parameters,
- Use blanks of zero air to confirm calibration,
- Instrument calibration data,
- Labeling of chromatograms - identify each chromatogram clearly by analysis type, injection volume, run number, date, and time,
- Replicate after every ten samples to check method/analyst precision, and
- Calibrate each day or after every eight hours of use, whichever comes first.

## **6. DATA VALIDATION**

Data should be reviewed to ensure that the QA/QC requirements listed above have been met.

## **7. HEALTH AND SAFETY**

Potentially hazardous materials will be tested. Ensure the work area has adequate ventilation and minimize contaminant exposure to exposed skin. Contaminated clothing should be thoroughly cleaned or disposed of.

## APPENDIX B

### SAMPLE CALCULATIONS AND CALIBRATION DATA

#### Sample Calculations

##### Concentrations

Concentrations are calculated by comparing the area of response to an area of a known concentration. If the response of a sample compound is 2200 mVs, and the response of a 10ppm compound at the same retention time is 2000 mVs, the concentration of the sample compound would be:

$$(2200\text{mVs} / 2000\text{mVs})(10\text{ppm}) = 11\text{ppm}$$

##### Calibration

One compound was used to conduct surrogate calibration in this project. The concentrations and retention times of all compounds in library are updated by use of this single calibration compound. Ratios of the retention time and response are used in updating. Assume the retention time and the response (10ppm) of the surrogate calibration compound is 60 seconds and 2000mVs respectively. When the calibration is run, the 10ppm sample produces a retention time of 66 seconds and a response of 2100mVs. The retention time and response for that compound become 66 seconds and 2100mVs respectively. All other compounds within the library then change by the ratio of:

$$66\text{sec} / 60\text{ sec} = 1.1, \text{ or}$$

$$(1.1)(\text{retention time for each compound}) = \text{new retention time for each compound; and}$$

$$2100\text{mVs} / 2000\text{mVs} = 1.05, \text{ or}$$

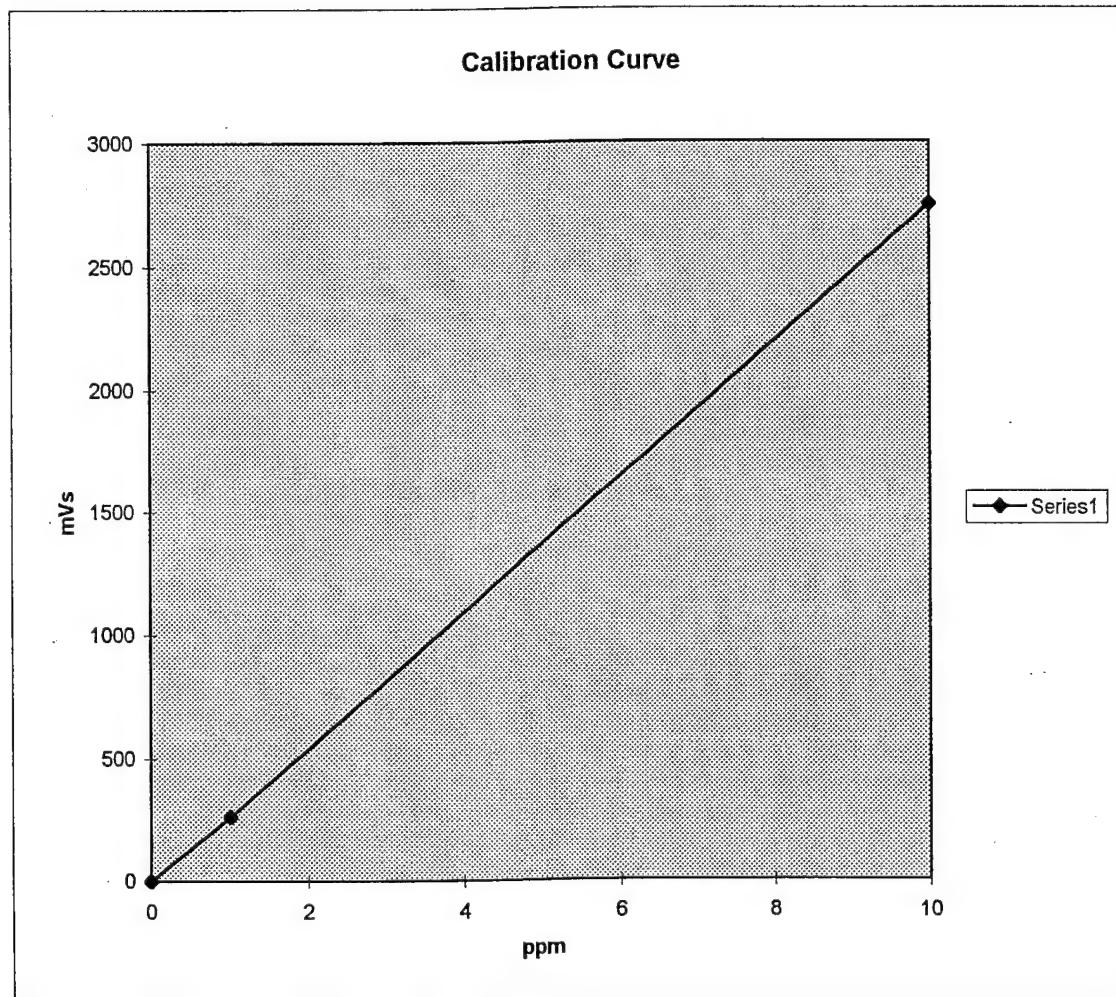
$$(1.05)(\text{response for each compound at 10ppm}) = \text{new response for each compound at 10ppm.}$$

**10.0 ppm Benzene**

Run	mVs	Standard Deviation	Average % from Average
1	2884	124.4307036	2747 4.987258828
2	2641		3.858755005
3	2716		1.128503822

**1.0 ppm Benzene**

Run	mVs	Standard Deviation	Average % from Average
1	274.8	12.05777757	263 4.486692015
2	250.7		4.676806084
3	263.5		0.190114068

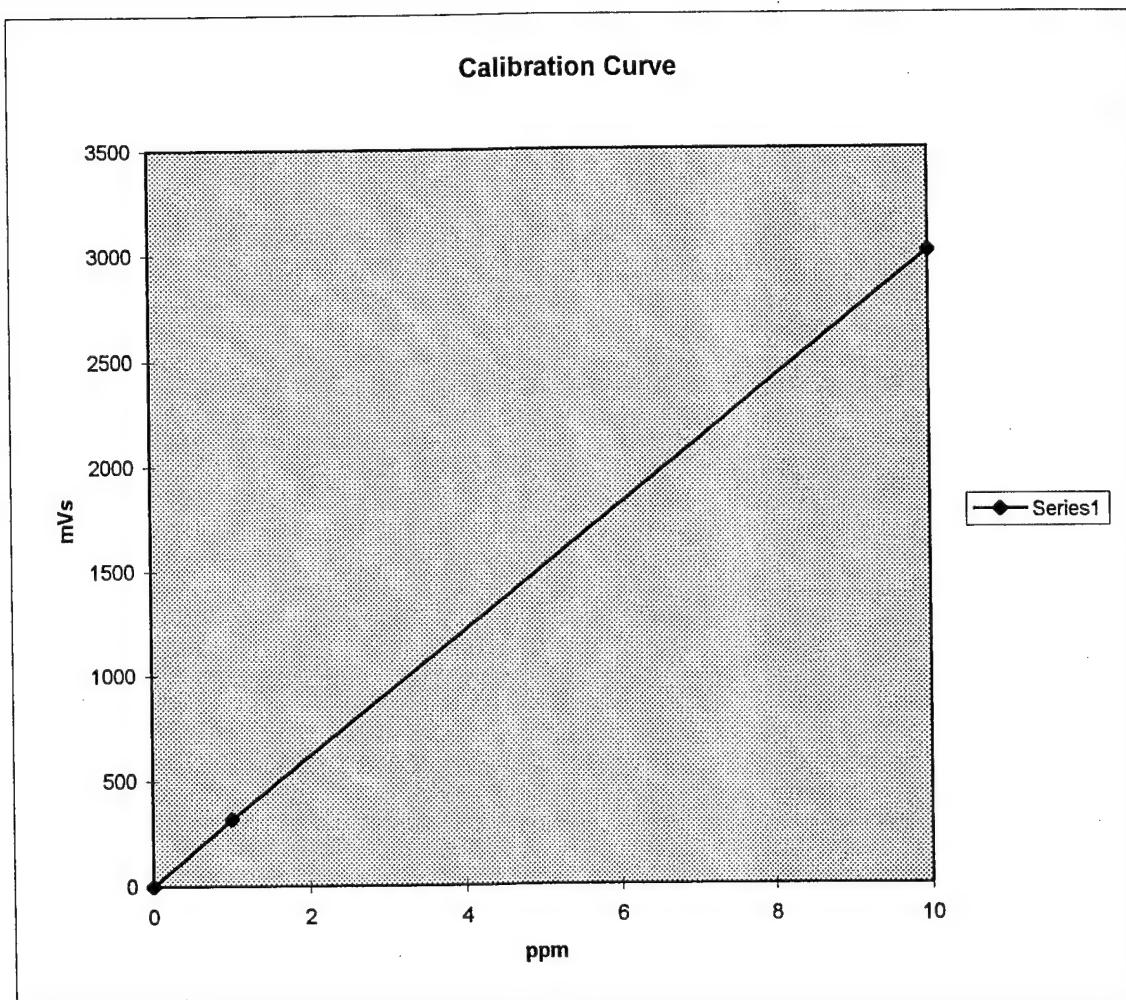


**10.0 ppm Trichloroethylene**

Run	mVs	Standard Deviation	Average	% from Average
1	3068	125.2836781	3008	1.994680851
2	2864			4.787234043
3	3092			2.792553191

**1.0 ppm Trichloroethylene**

Run	mVs	Standard Deviation	Average	% from Average
1	327.8	7.52861209	319.2	2.694235589
2	316			1.002506266
3	313.8			1.691729323

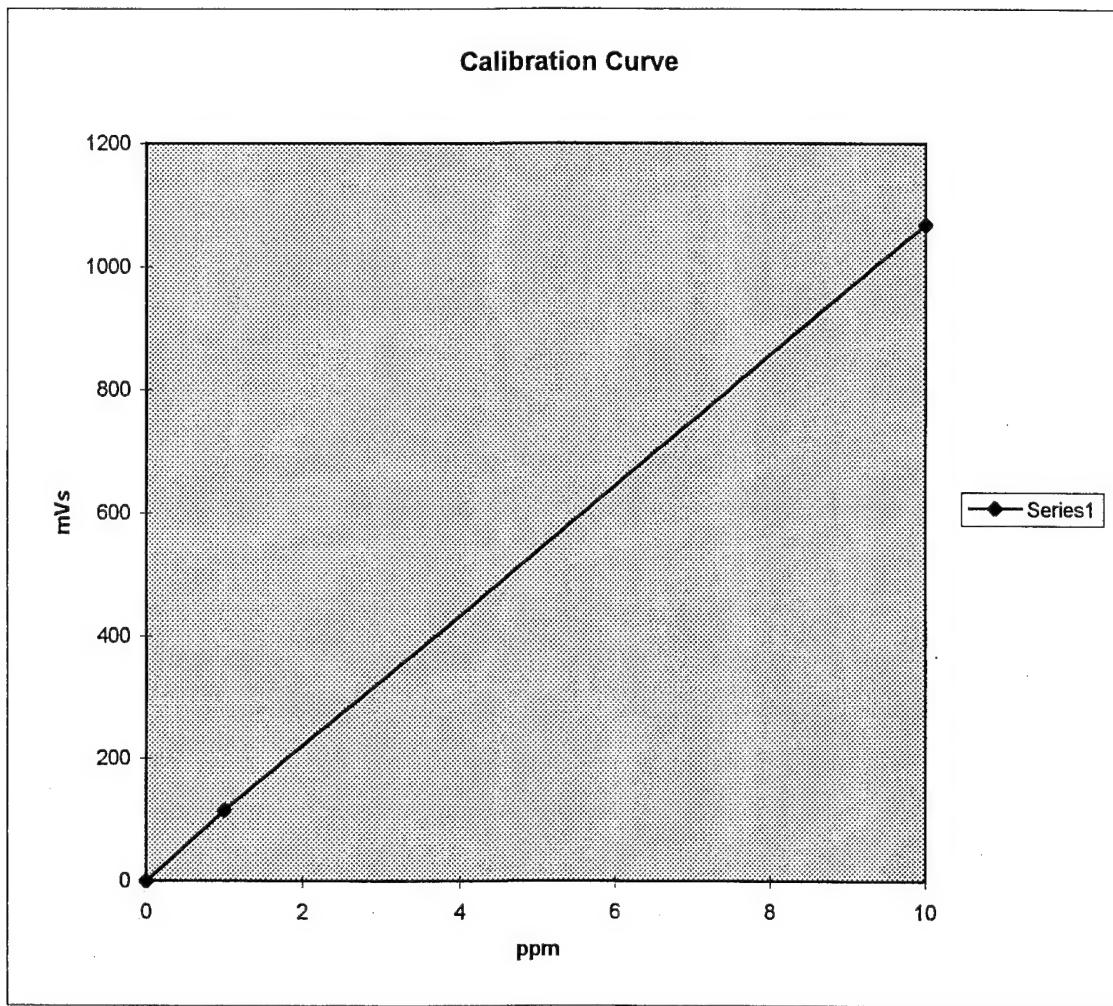


**10.0 ppm Toluene**

Run	mVs	Standard Deviation	Average	% from Average
1	1023	44.57577818	1069	4.303086997
2	1112			4.022450889
3	1072			0.280636109

**1.0 ppm Toluene**

Run	mVs	Standard Deviation	Average	% from Average
1	118.9	4.927473998	114.3	4.024496938
2	109.1			4.549431321
3	114.9			0.524934383

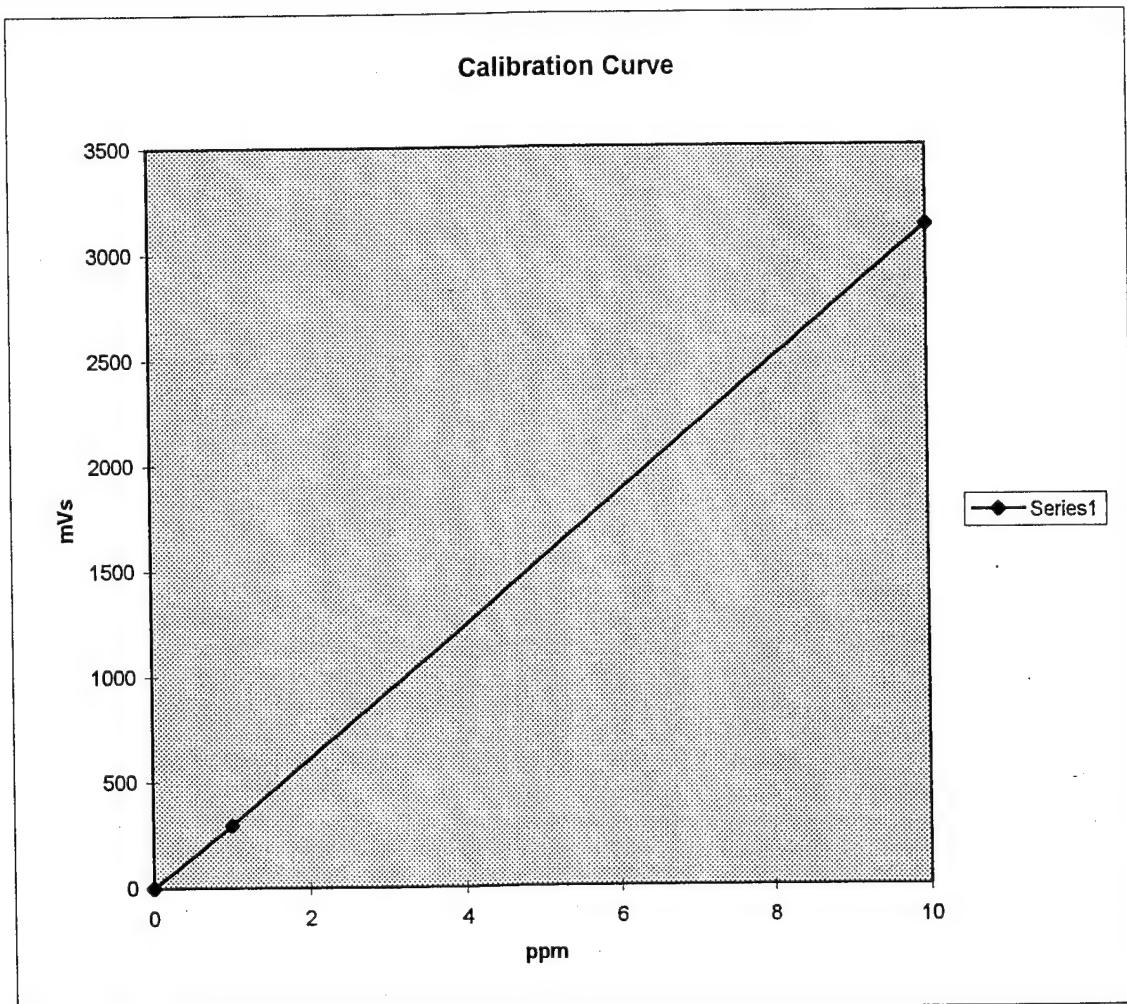


**10.0 ppm Tetrachloroethylene**

Run	mVs	Standard Deviation	Average	% from Average
1	3269	148.040535	3123	4.674991995
2	3127			0.128081972
3	2973			4.803073967

**1.0 ppm Tetrachloroethylene**

Run	mVs	Standard Deviation	Average	% from Average
1	301.9	9.865596789	295	2.338983051
2	283.7			3.830508475
3	299.4			1.491525424

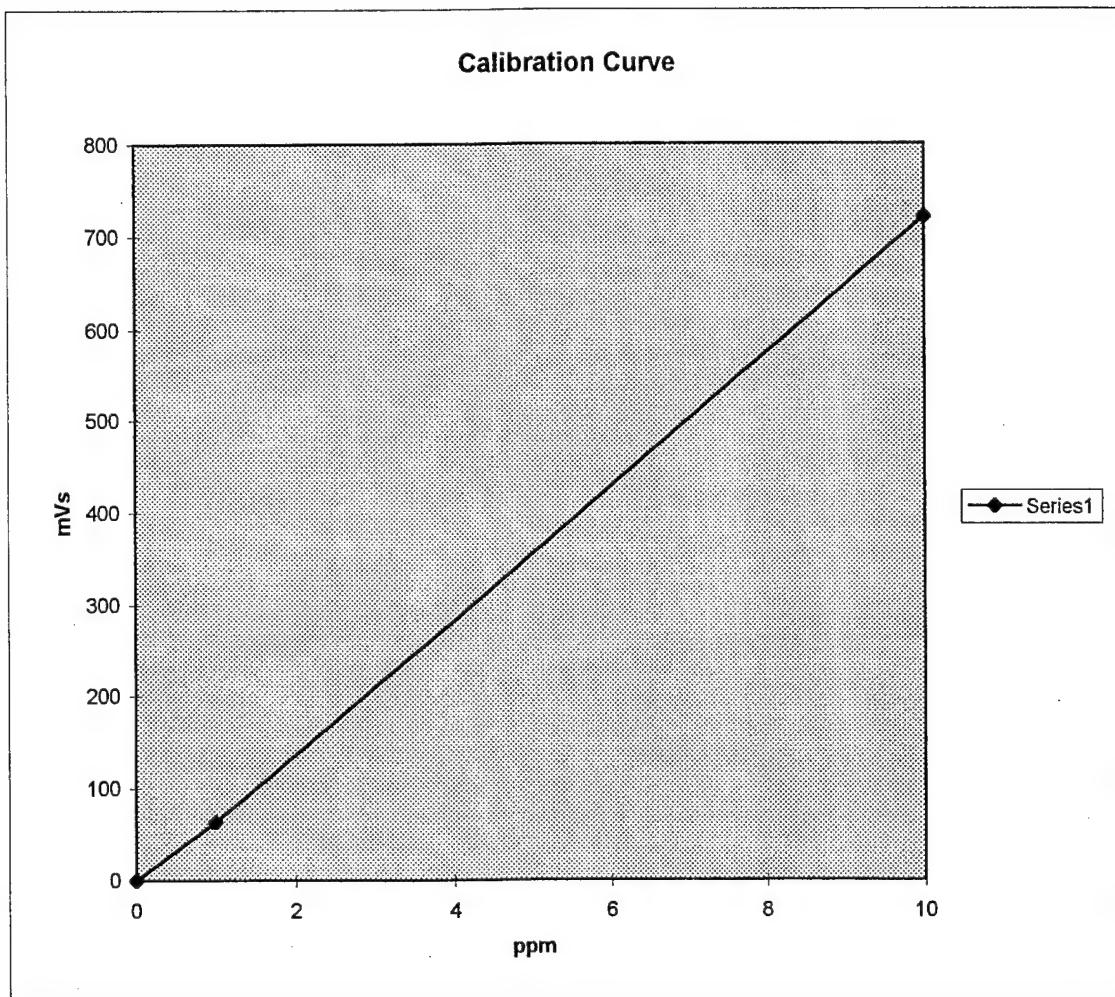


**10.0 ppm Ethylbenzene**

Run	mVs	Standard Deviation	Average	% from Average
1	738.7	19.67231557	720.7	2.497571805
2	699.7			2.913833773
3	723.7			0.416261968

**1.0 ppm Ethylbenzene**

Run	mVs	Standard Deviation	Average	% from Average
1	65.54	1.930077719	63.32	3.506001263
2	62.38			1.484523057
3	62.04			2.021478206



**10.0 ppm m - & p - Xylenes**

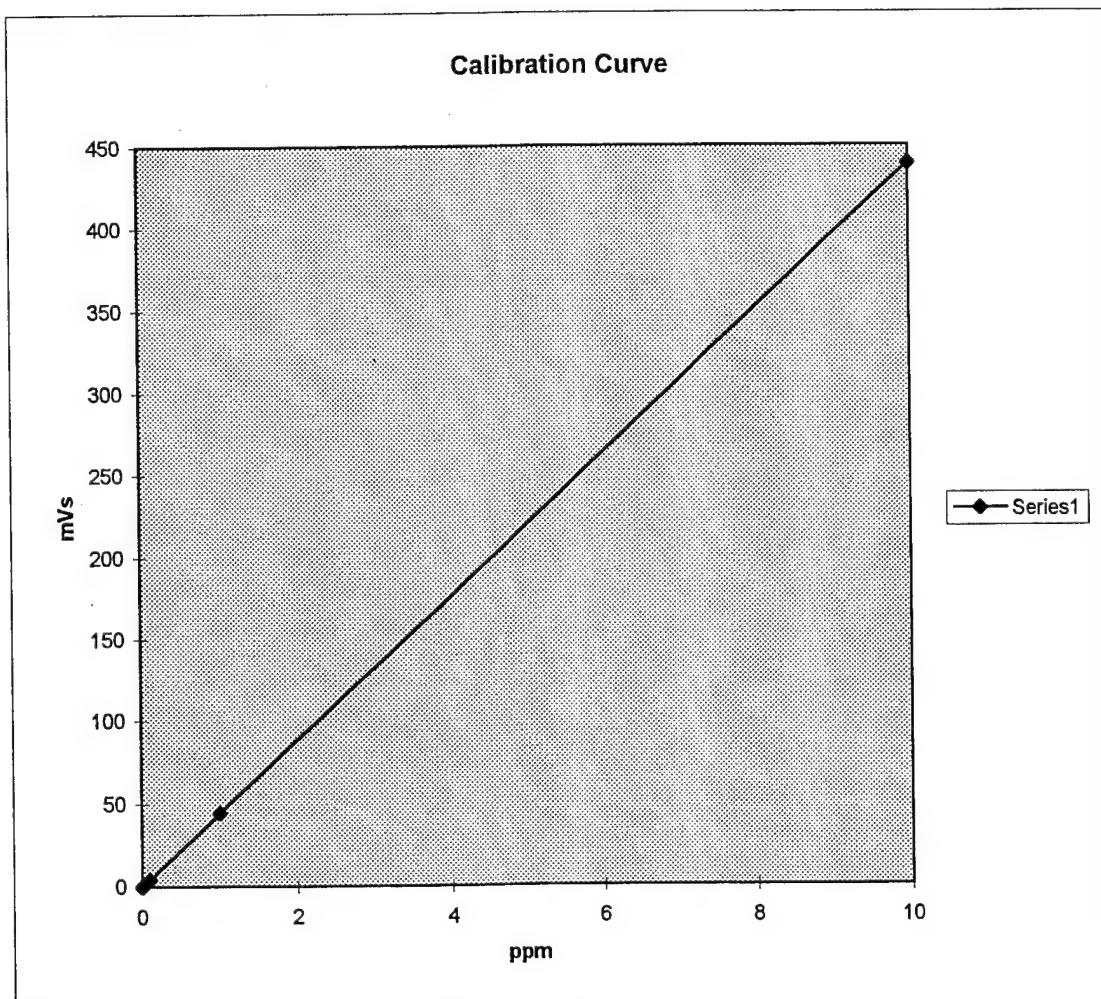
Run	mVs	Standard Deviation	Average	% from Average
1	452.2	14.86371421	439	3.006833713
2	422.9			3.667425968
3	441.9			0.660592255

**1.0 ppm m - & p - Xylenes**

Run	mVs	Standard Deviation	Average	% from Average
1	43.5	1.362938003	44.46	2.159244265
2	46.02			3.50877193
3	43.86			1.349527665

**0.1 ppm m - & p - Xylenes**

Run	mVs	Standard Deviation	Average	% from Average
1	4.399	0.15018988	4.356	0.987144169
2	4.189			3.83379247
3	4.48			2.846648301



**10.0 ppm o - Xylenes**

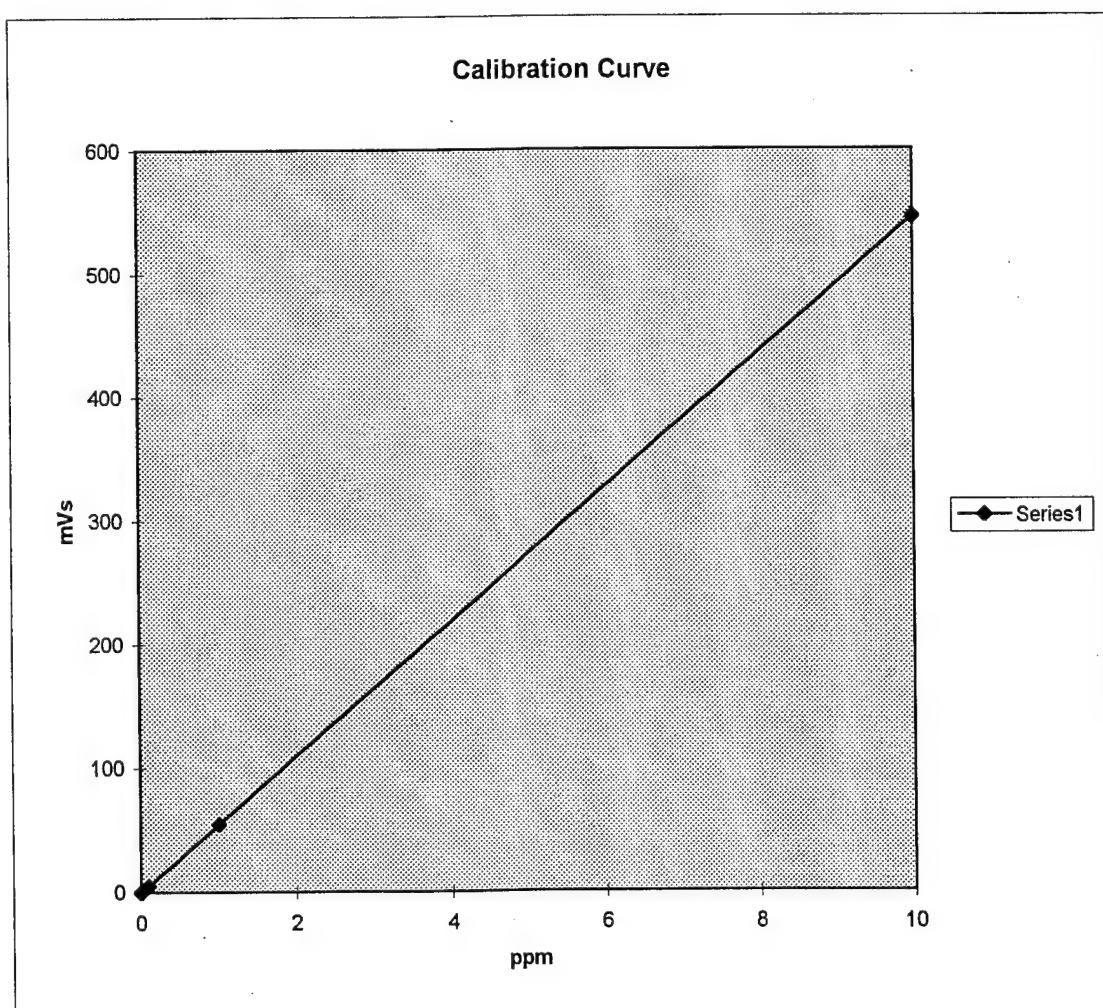
Run	mVs	Standard Deviation	Average	% from Average
1	567.4	19.03129002	545.6	3.995601173
2	532.3			2.437683284
3	537.1			1.557917889

**1.0 ppm o - Xylenes**

Run	mVs	Standard Deviation	Average	% from Average
1	56.8	1.683686432	54.86	3.536274152
2	54			1.567626686
3	53.78			1.968647466

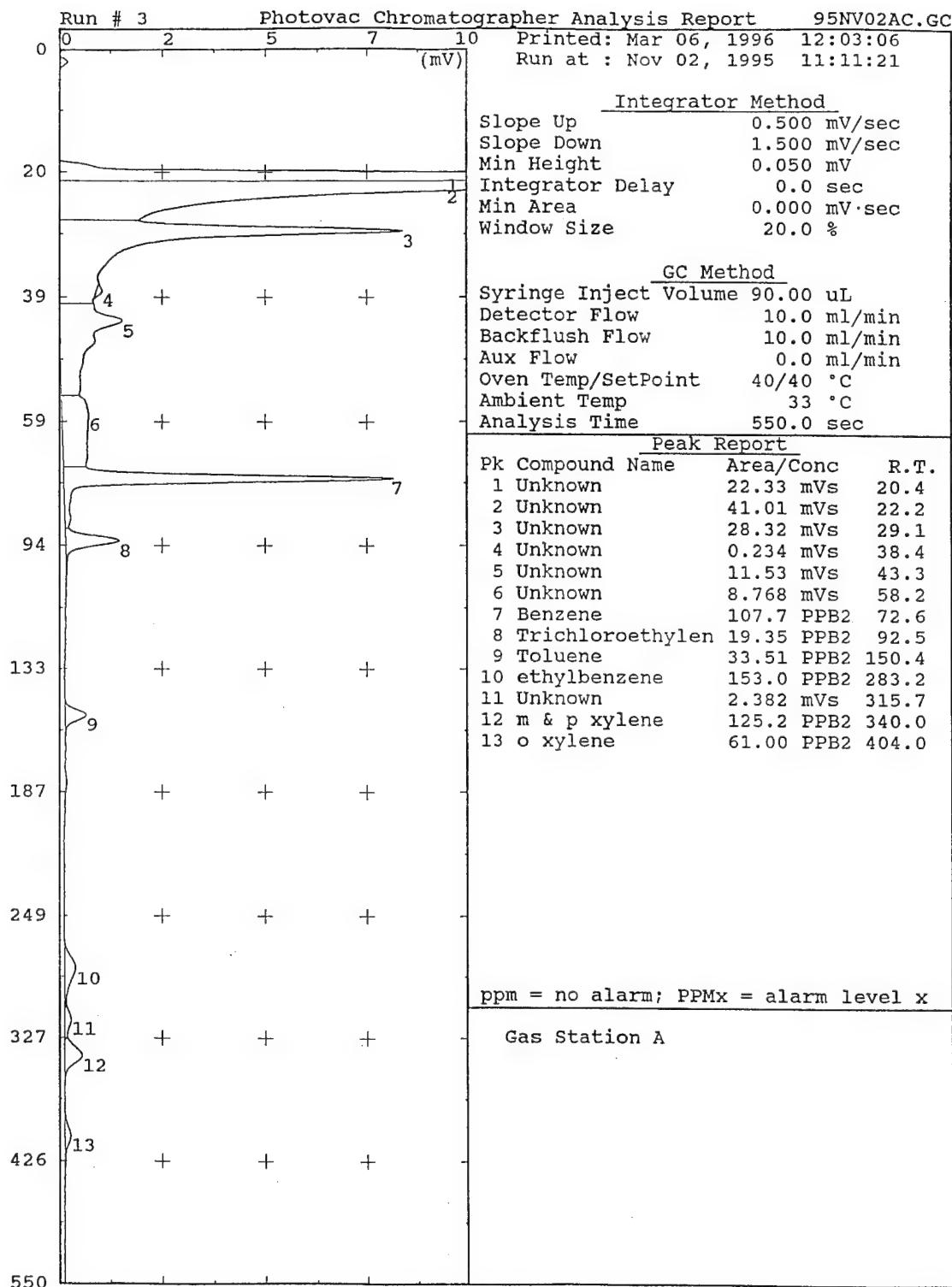
**0.1 ppm o - Xylenes**

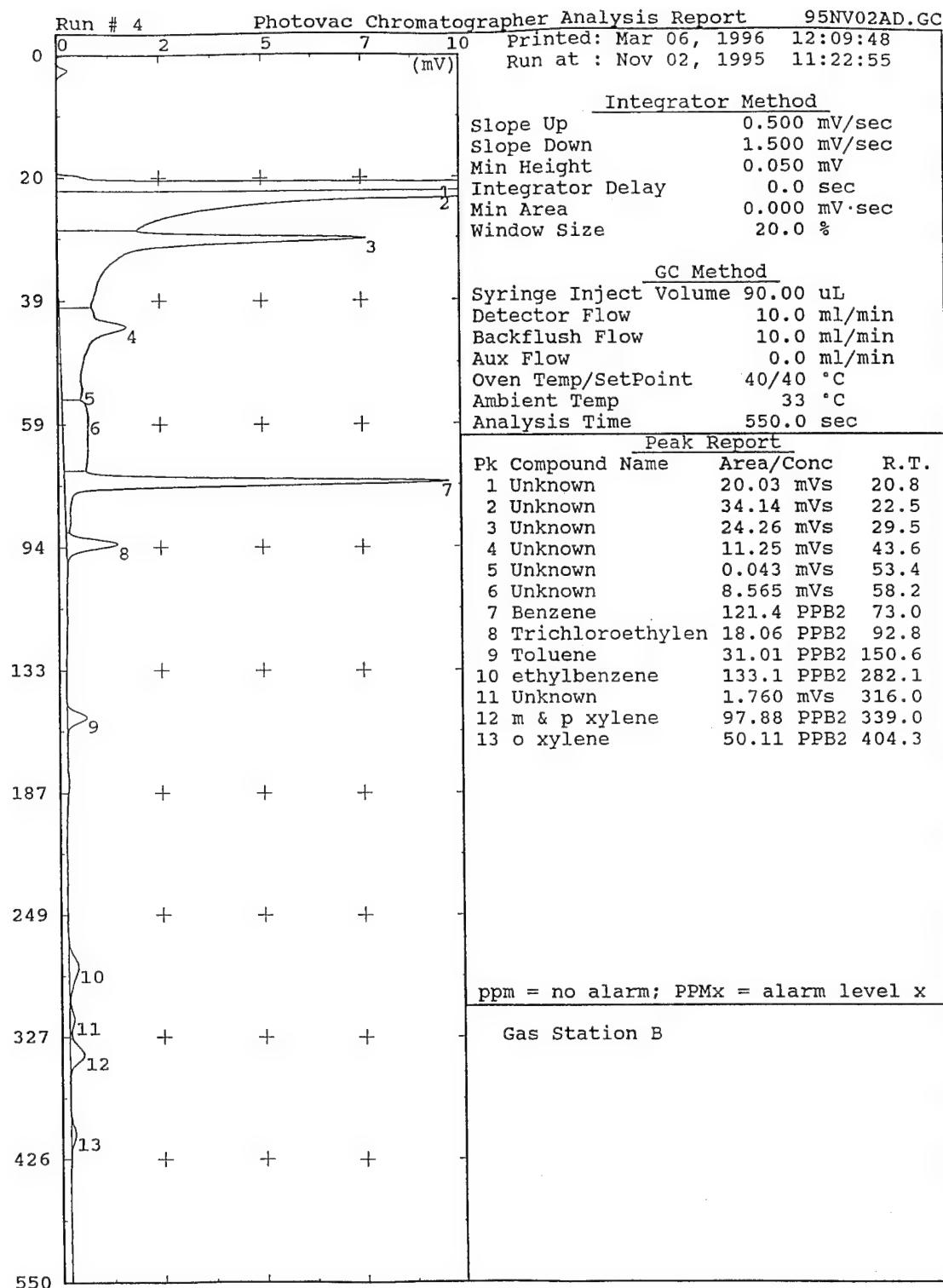
Run	mVs	Standard Deviation	Average	% from Average
1	5.229	0.17185168	5.078	2.973611658
2	4.891			3.682552186
3	5.114			0.708940528

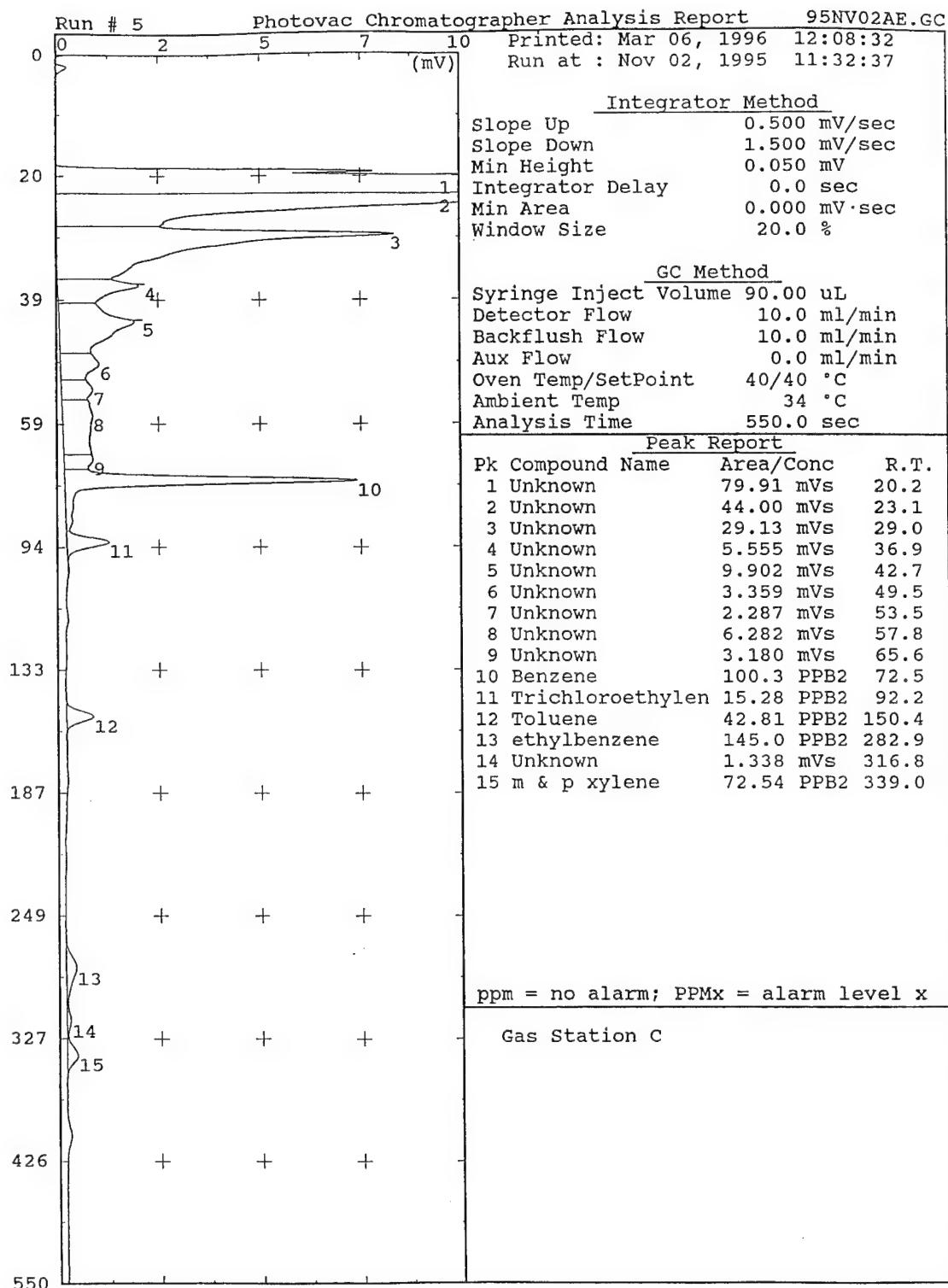


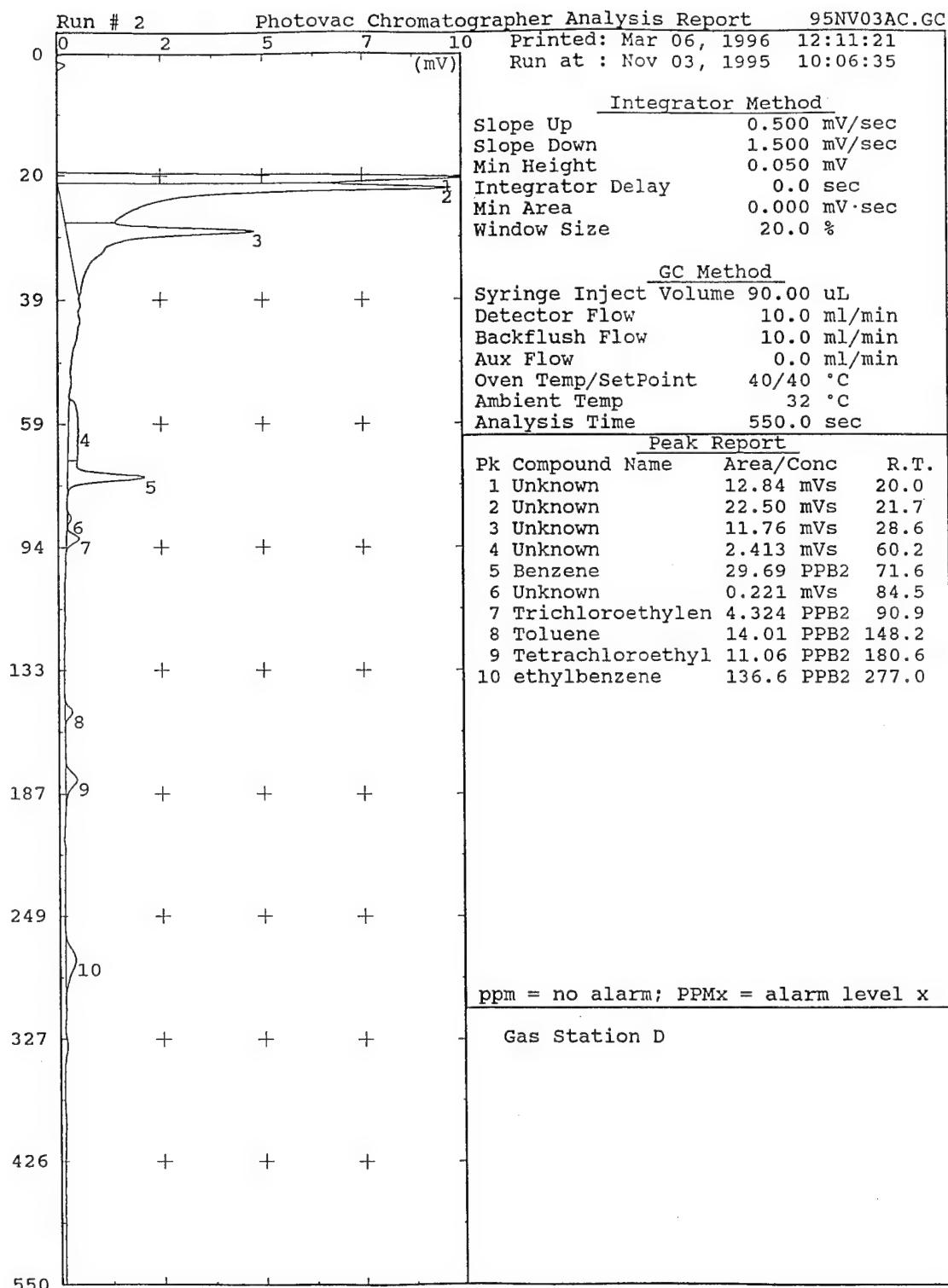
**APPENDIX C**

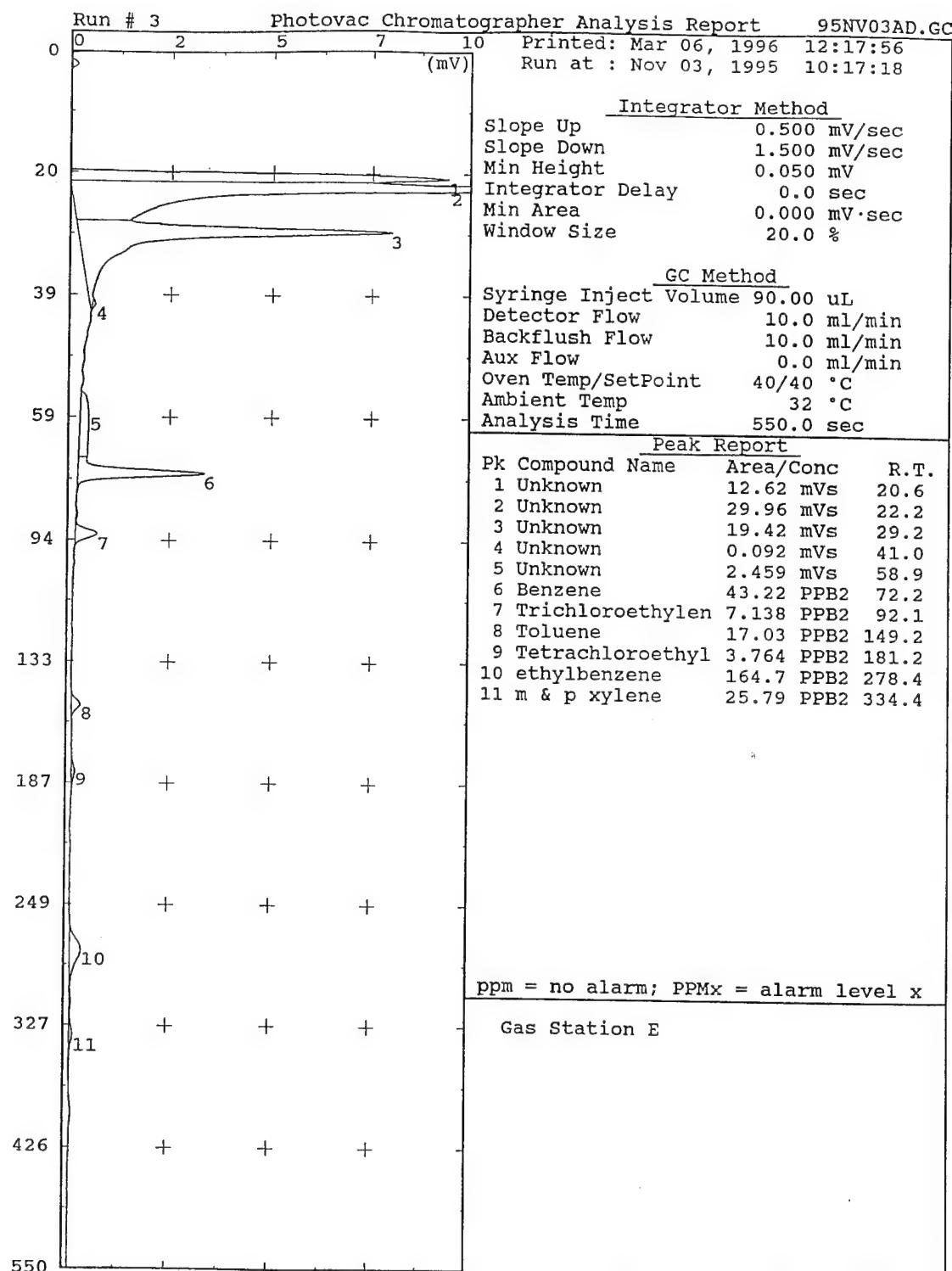
**GAS STATION CHROMATOGRAMS**

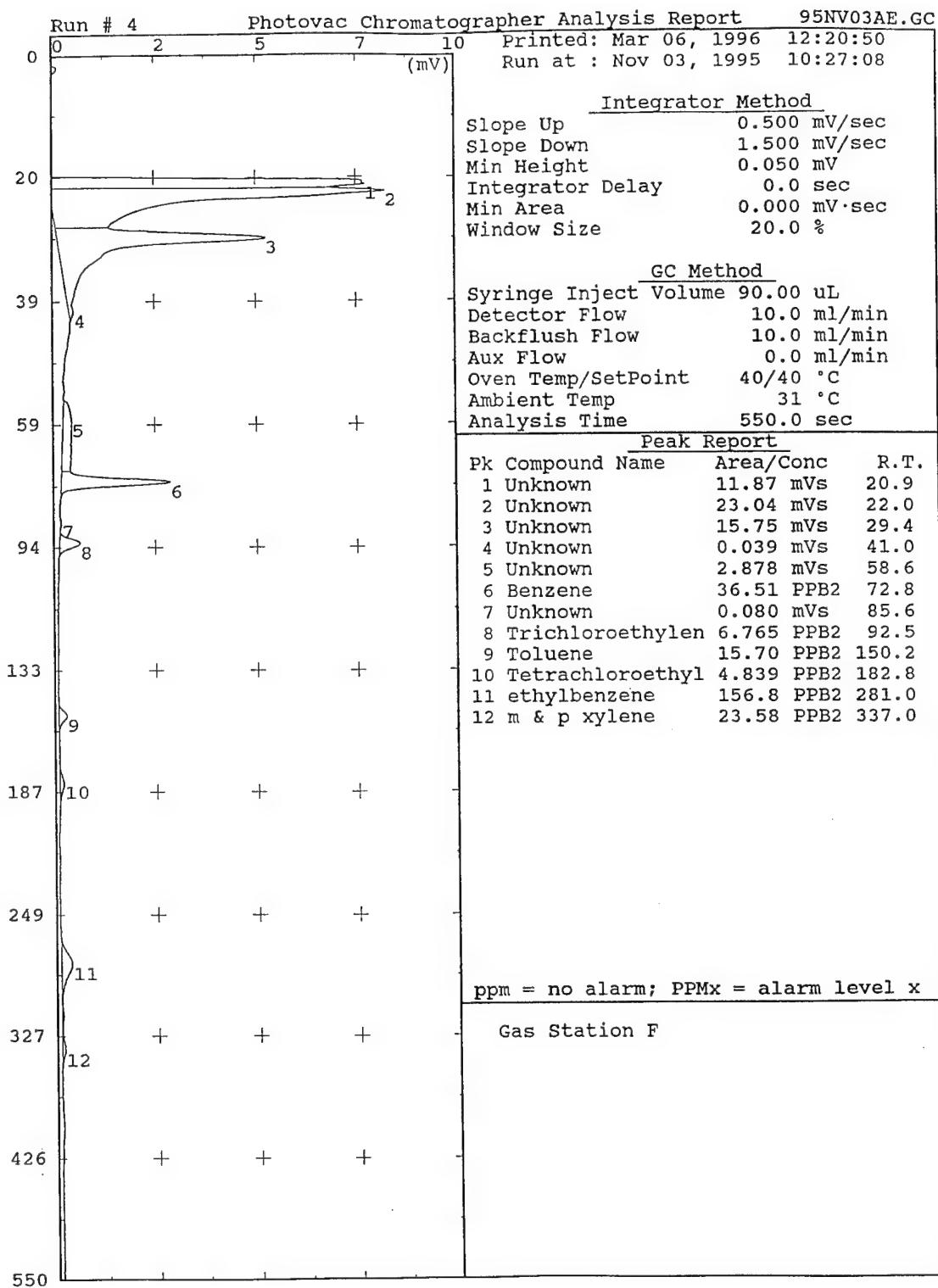


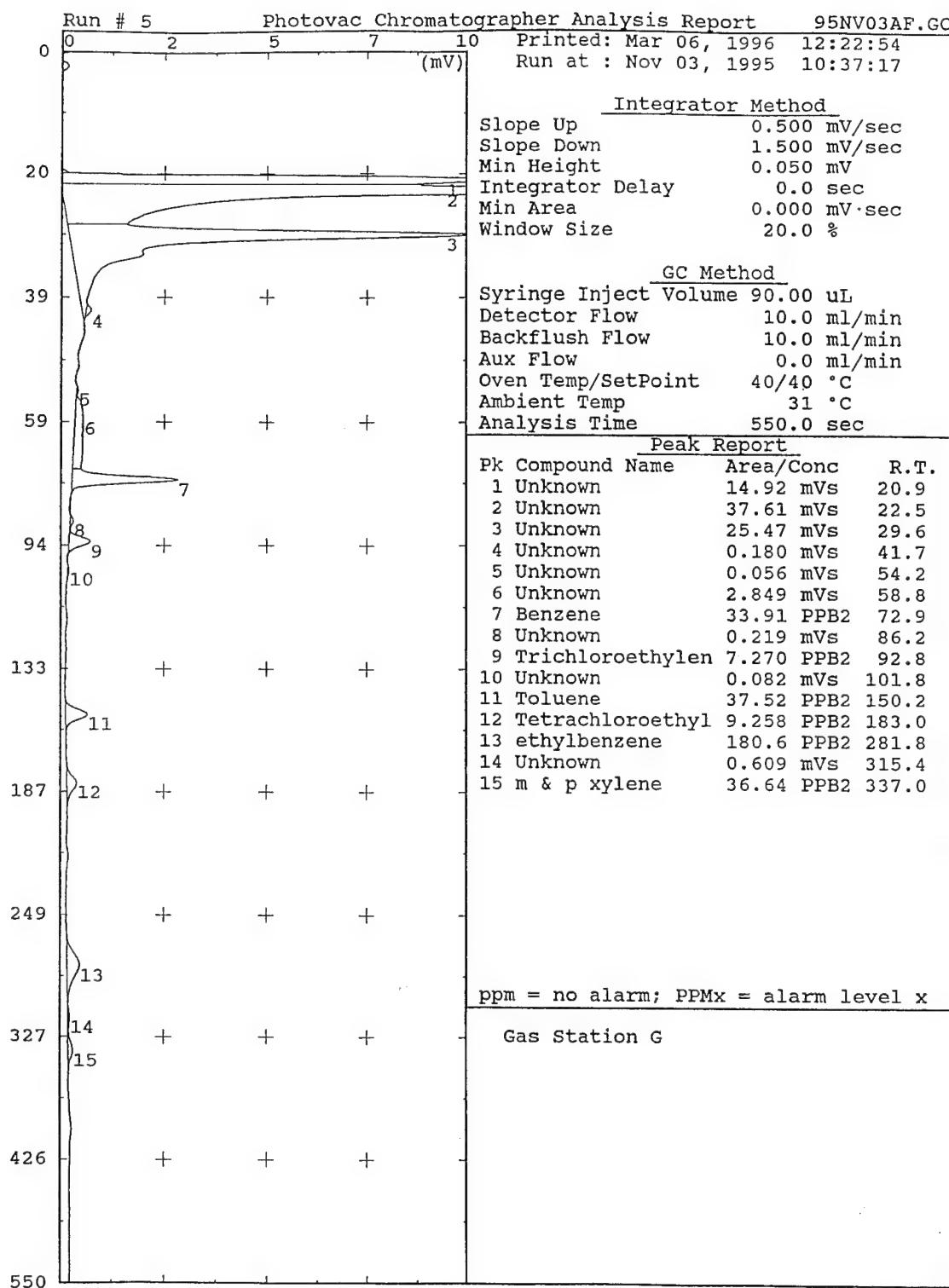


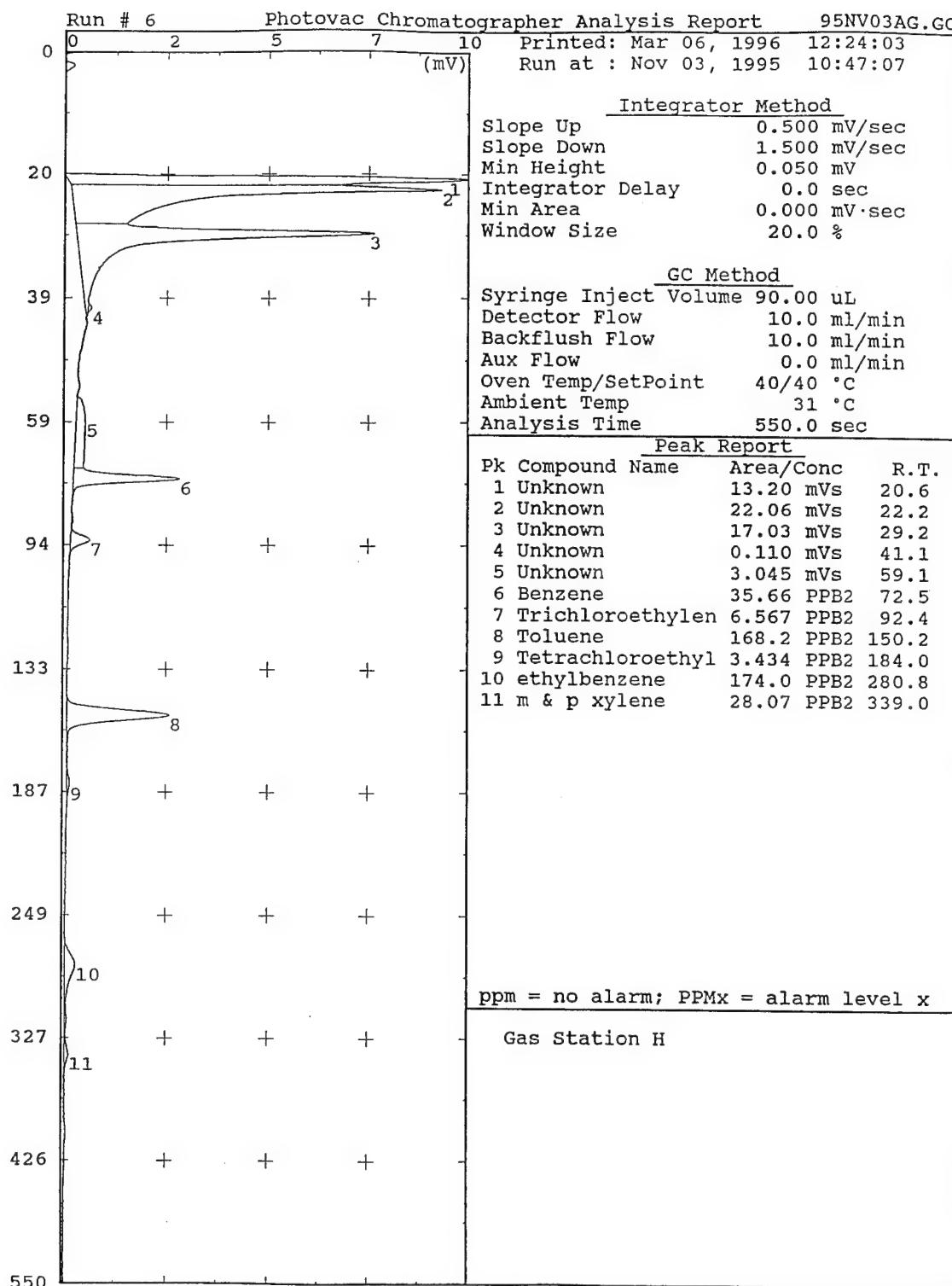


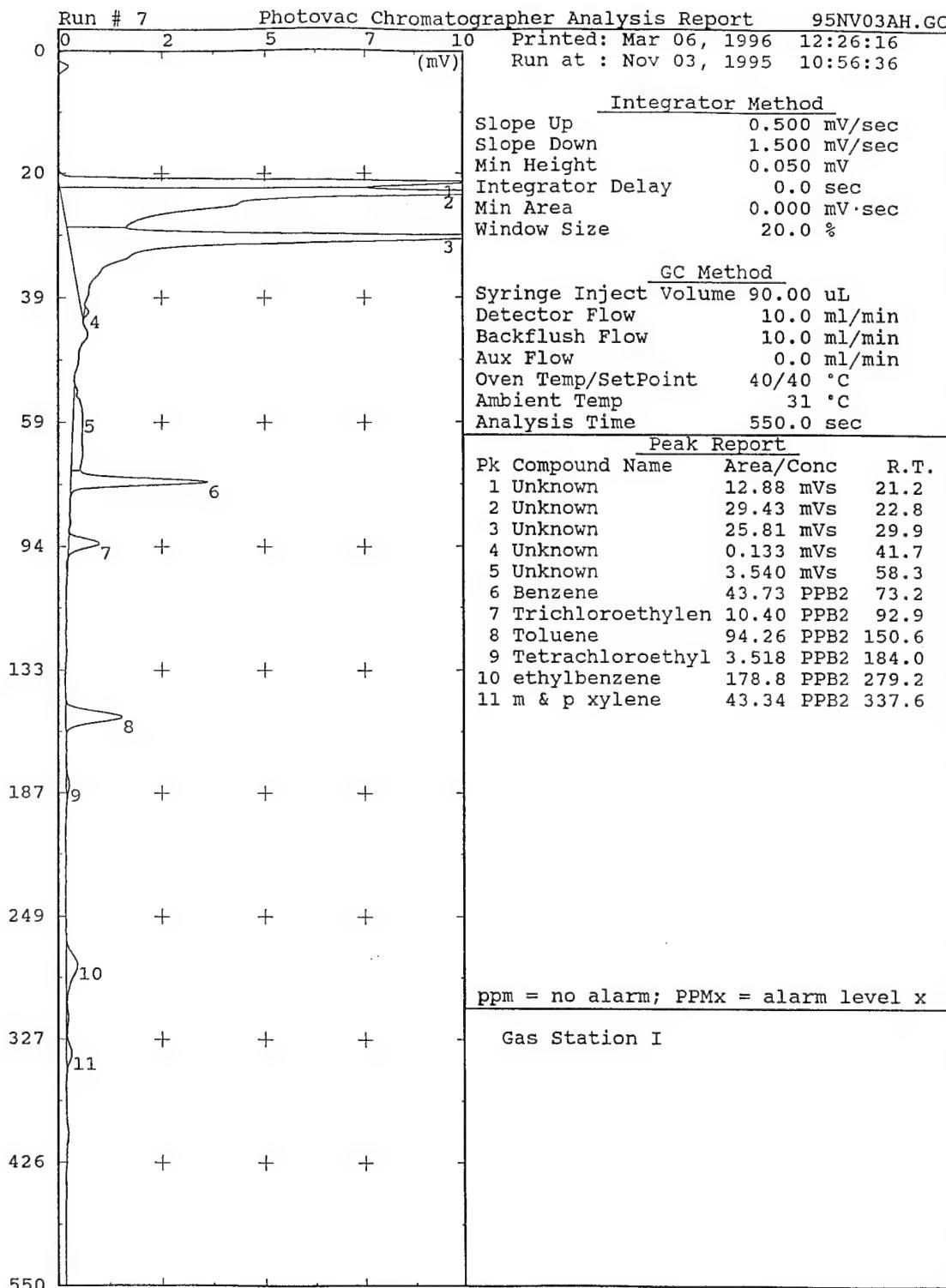


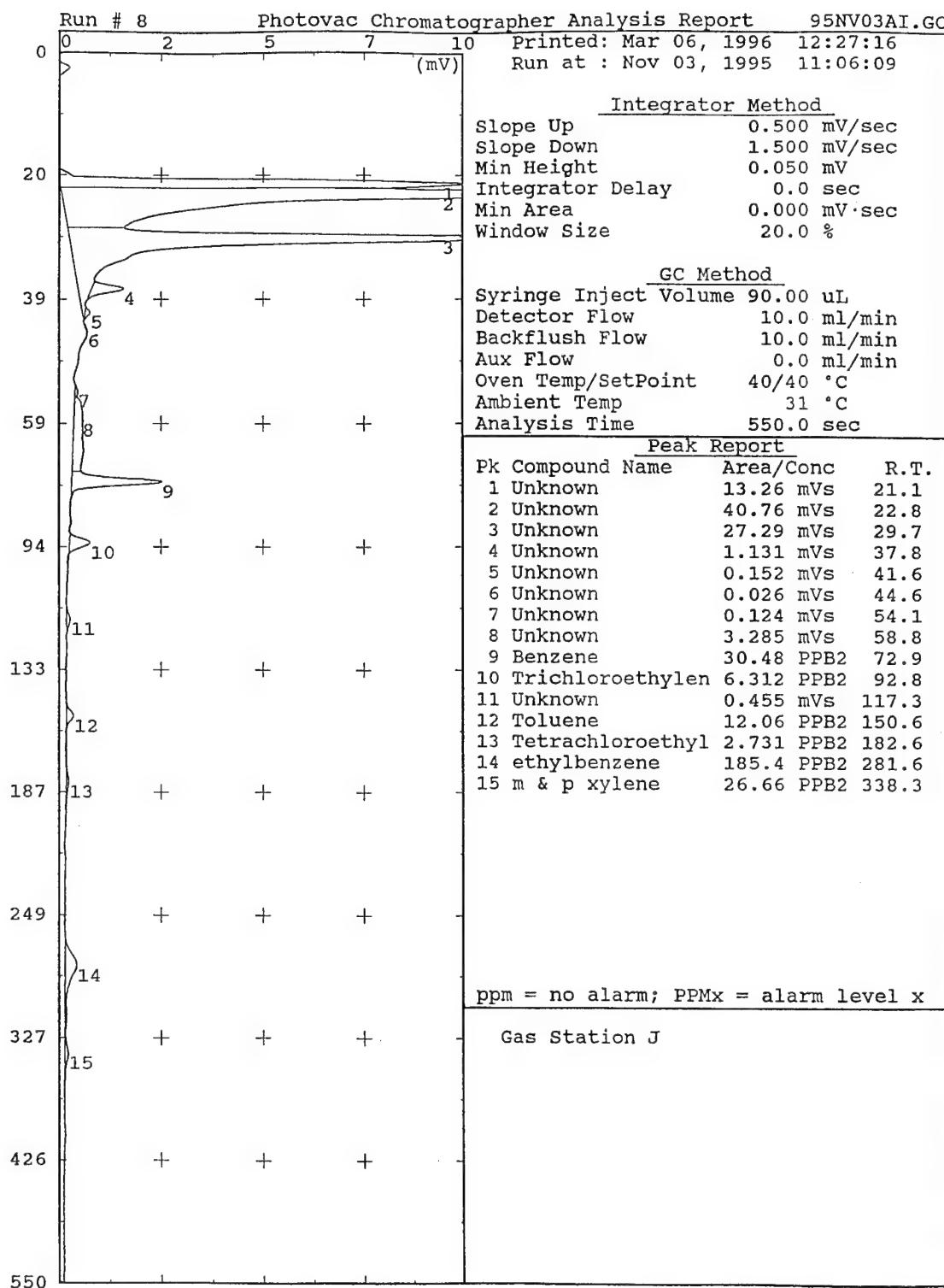


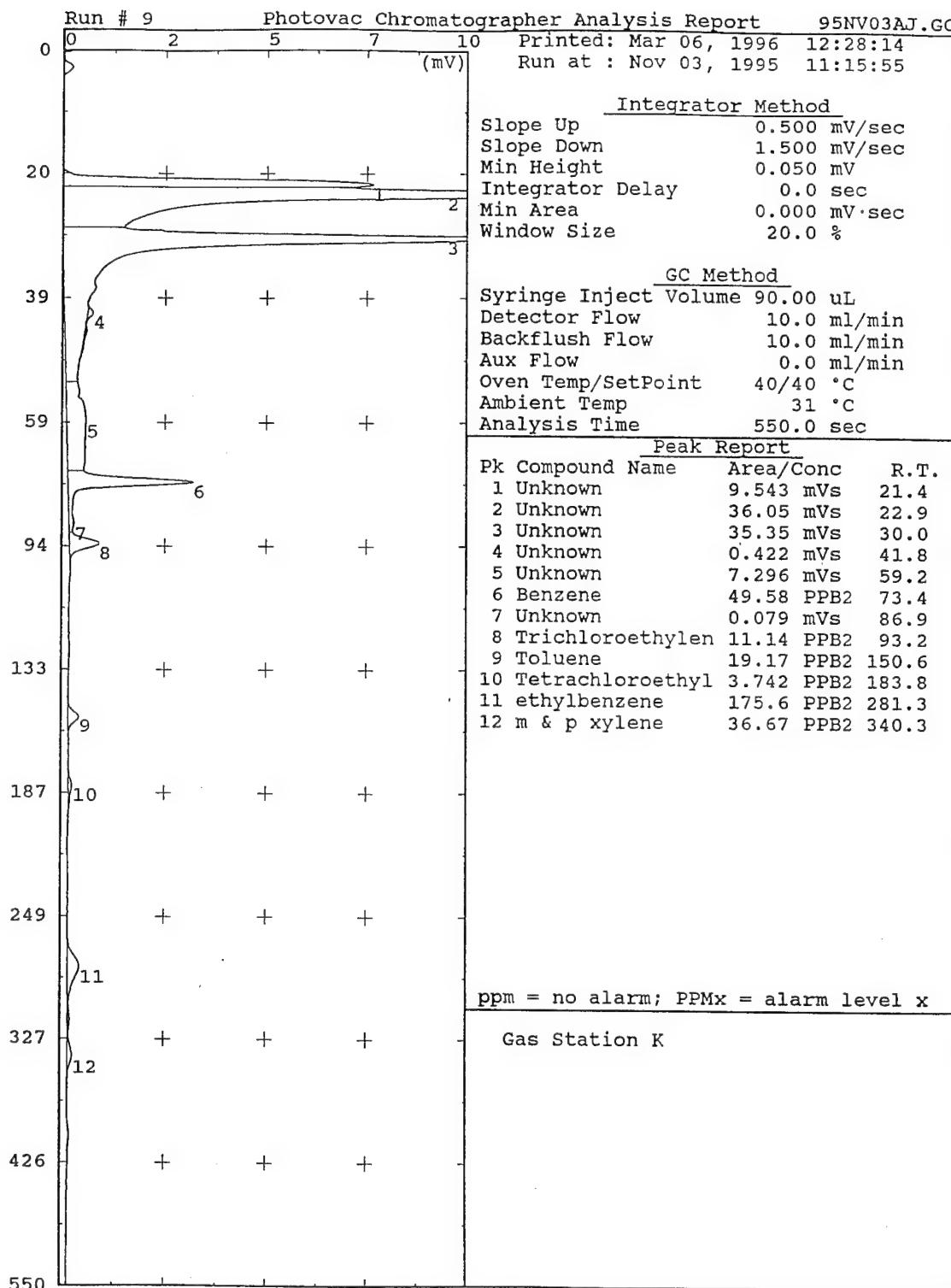


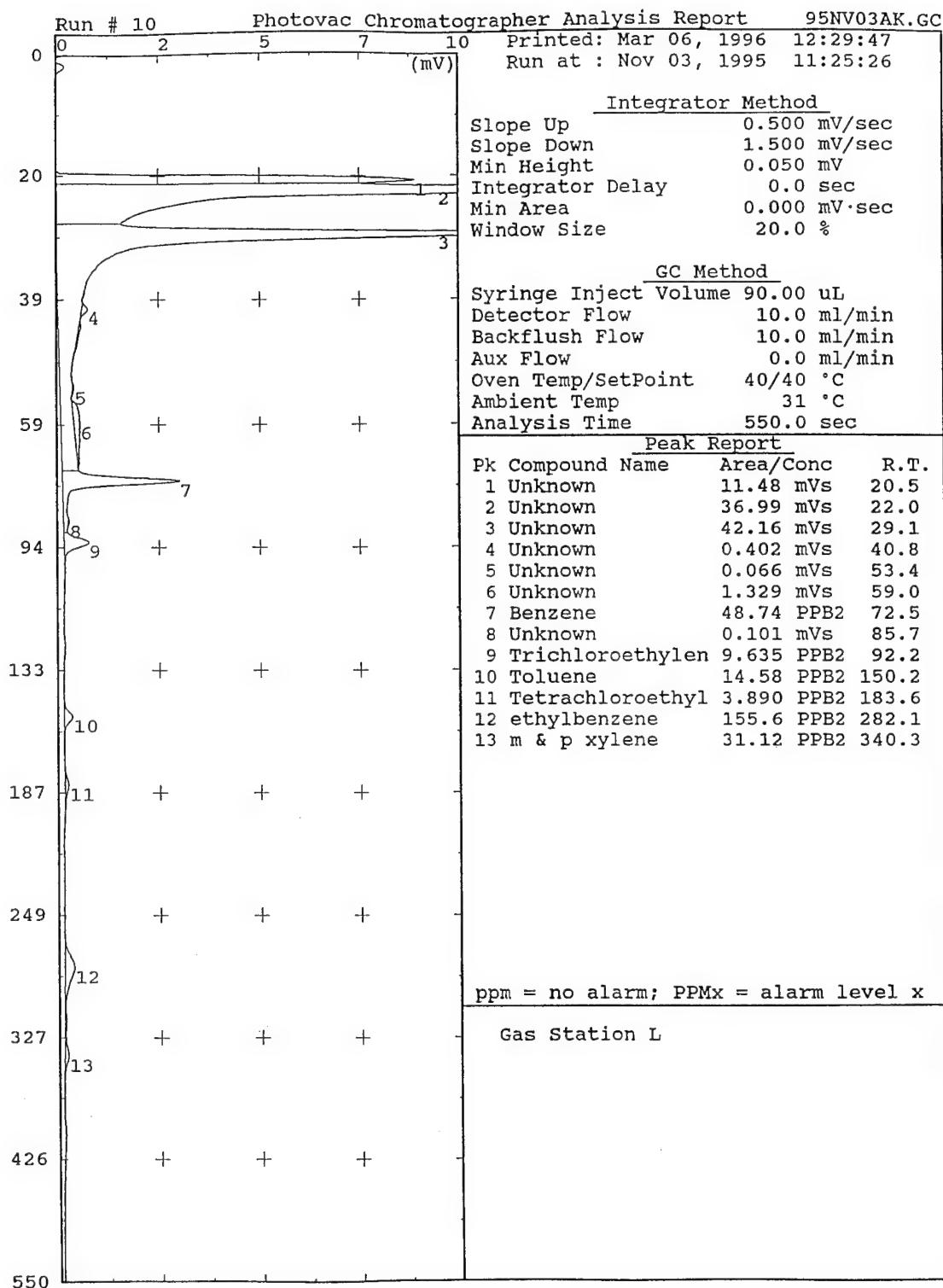


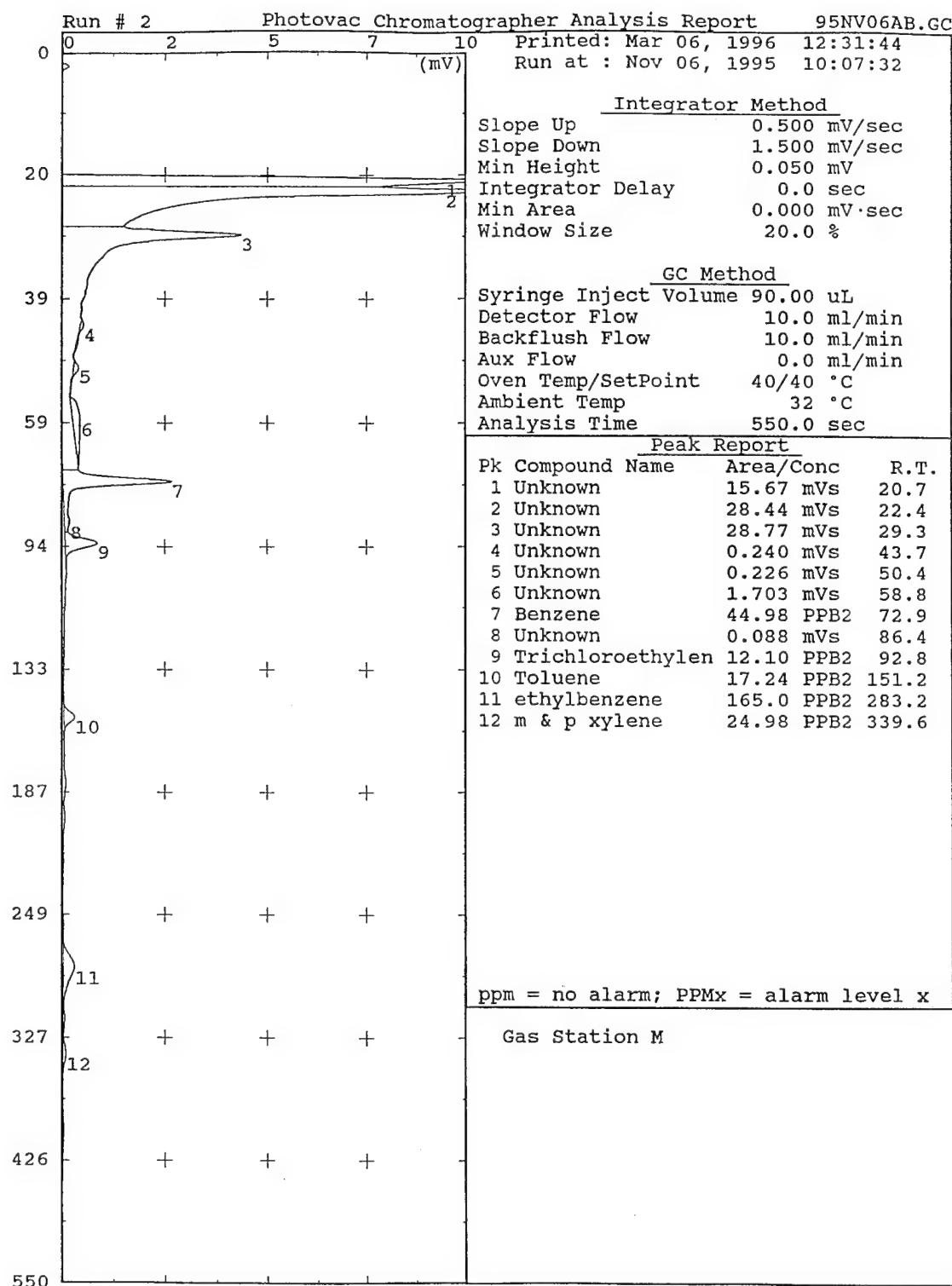


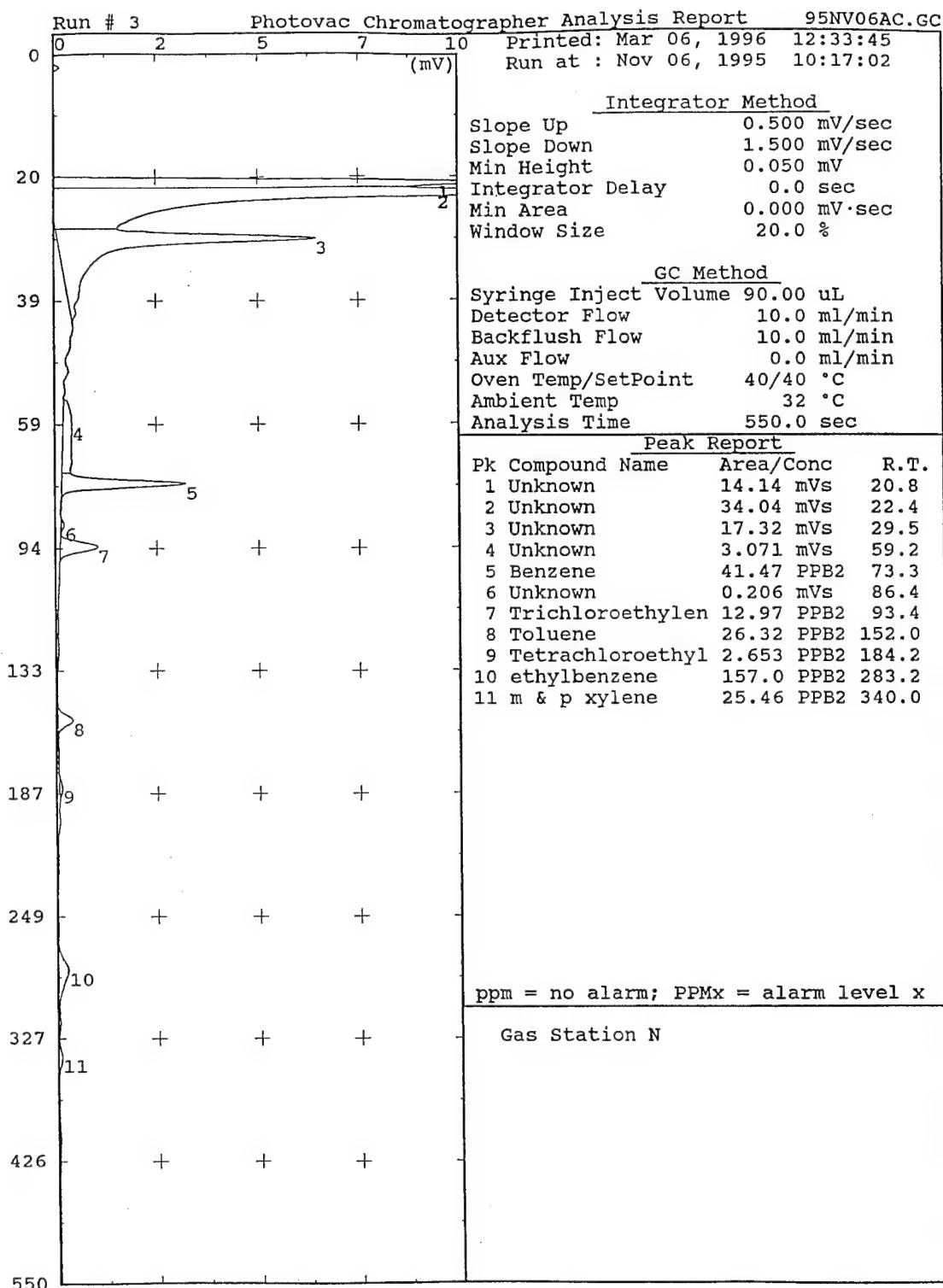


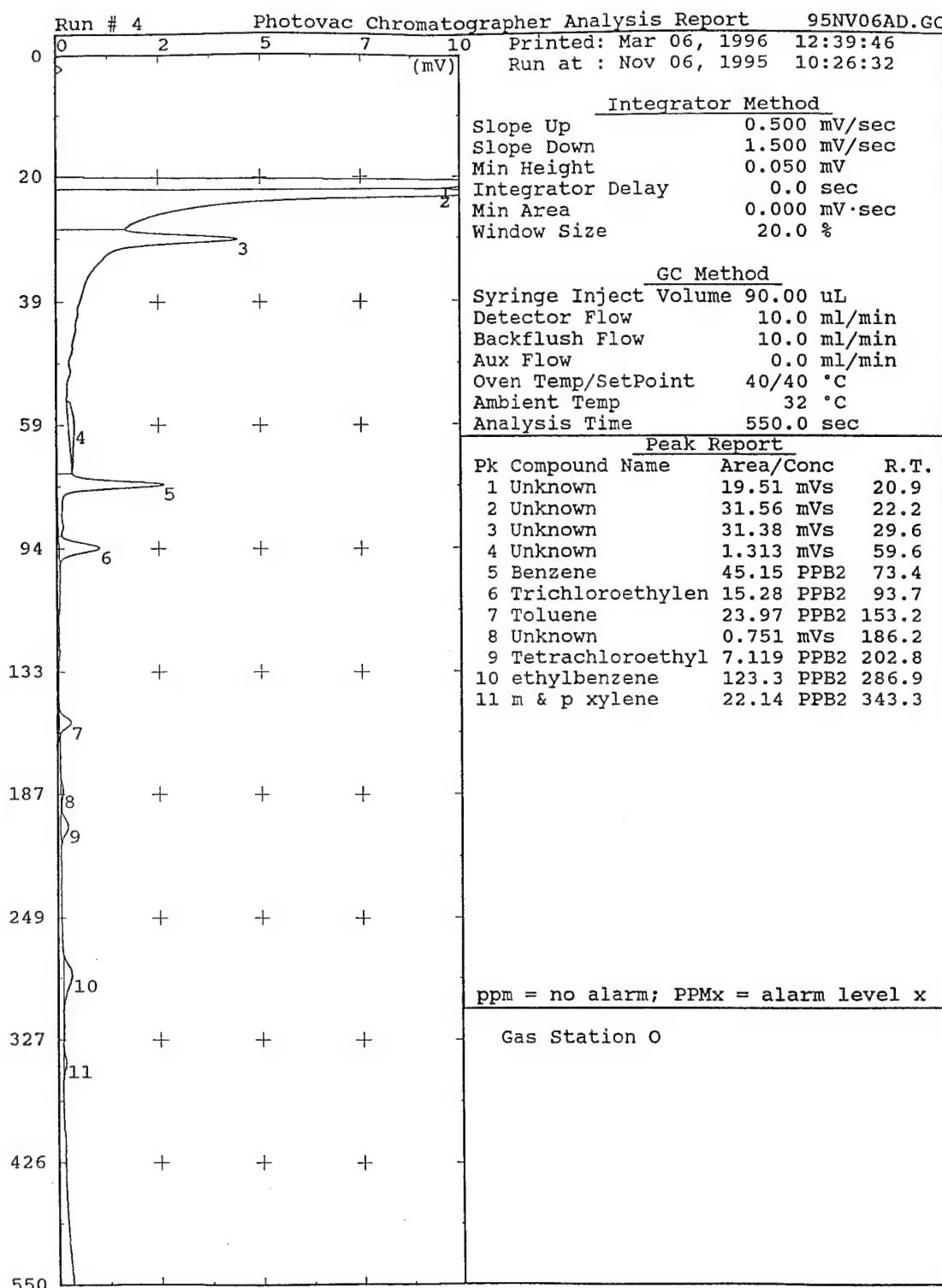


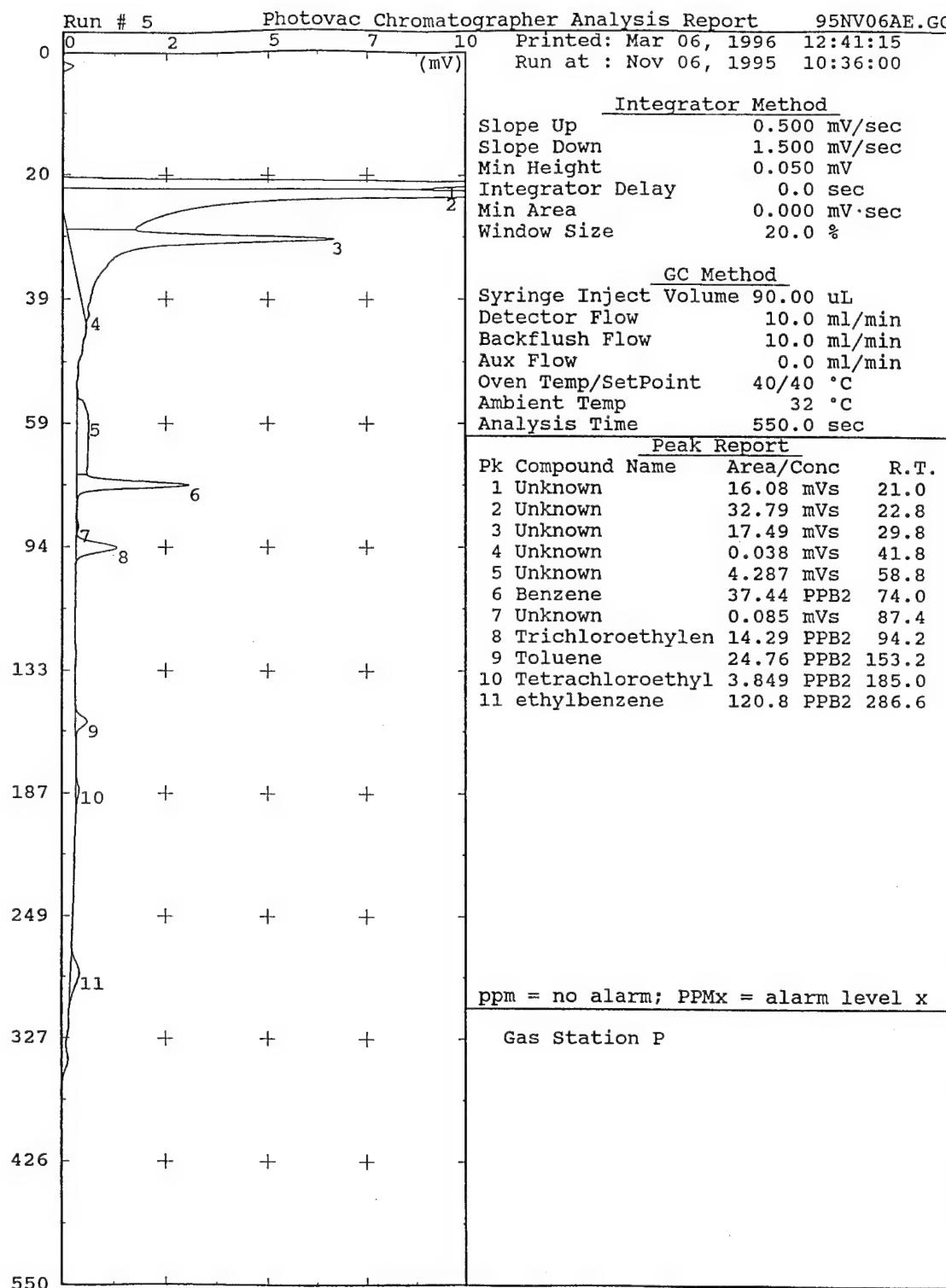


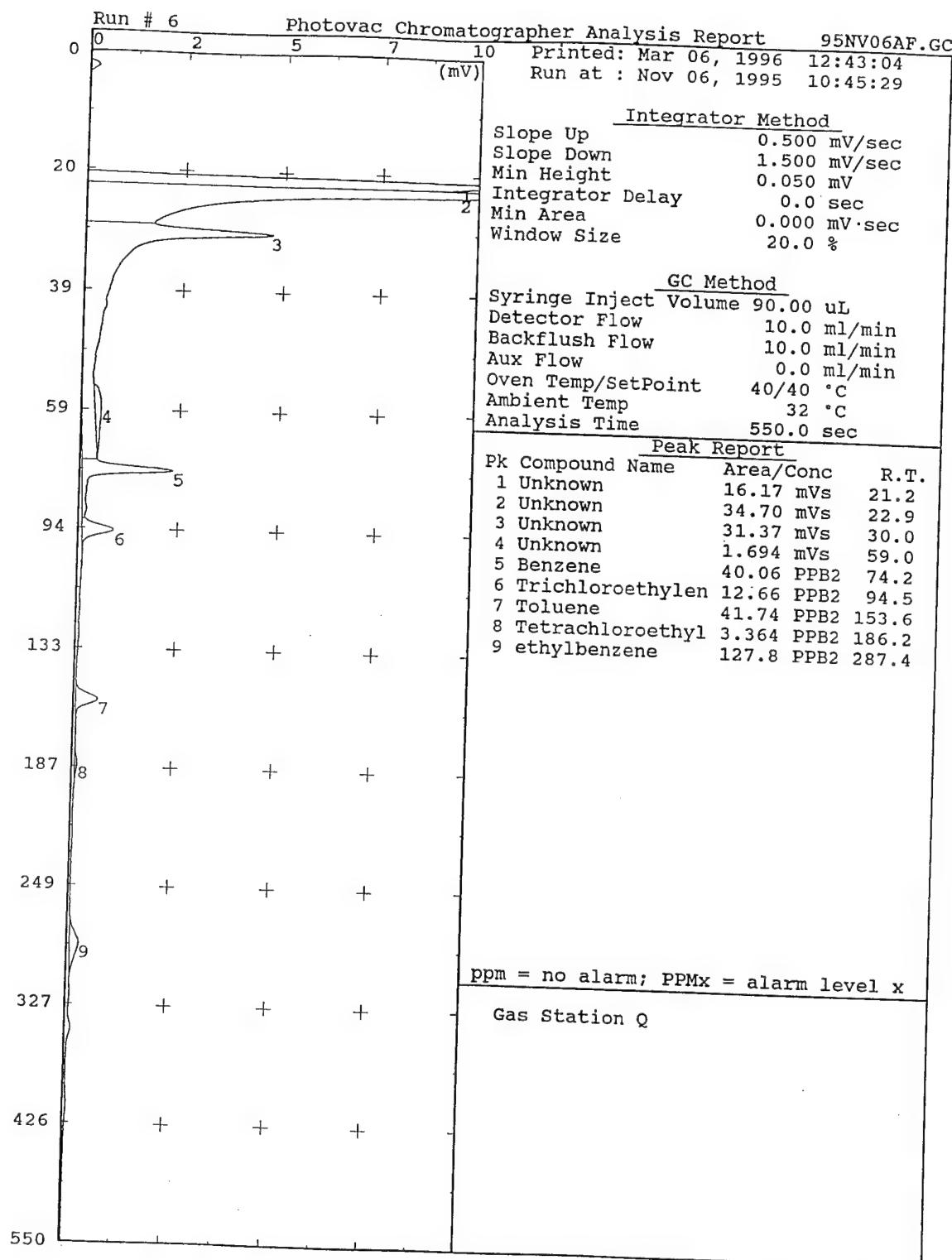


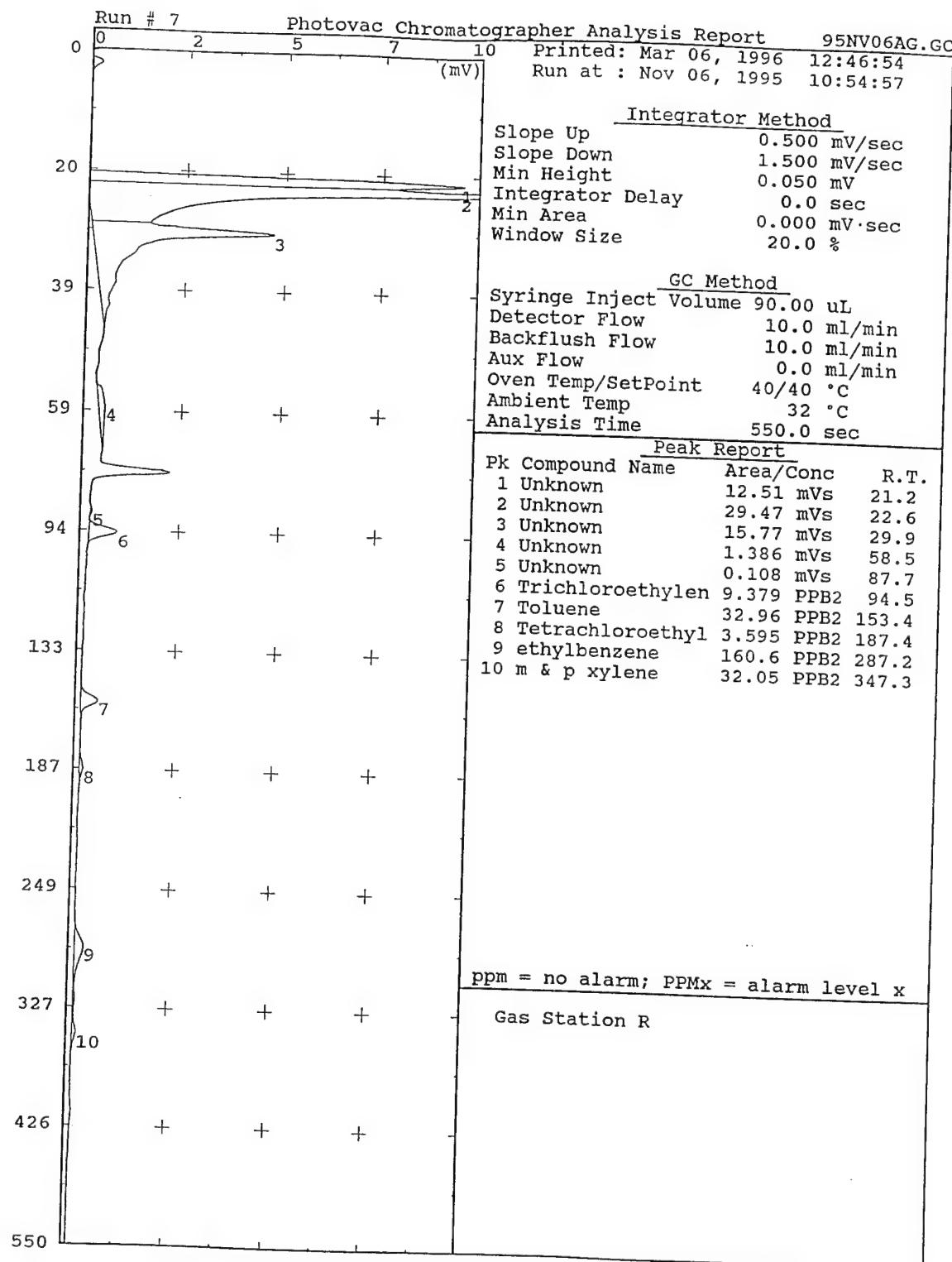


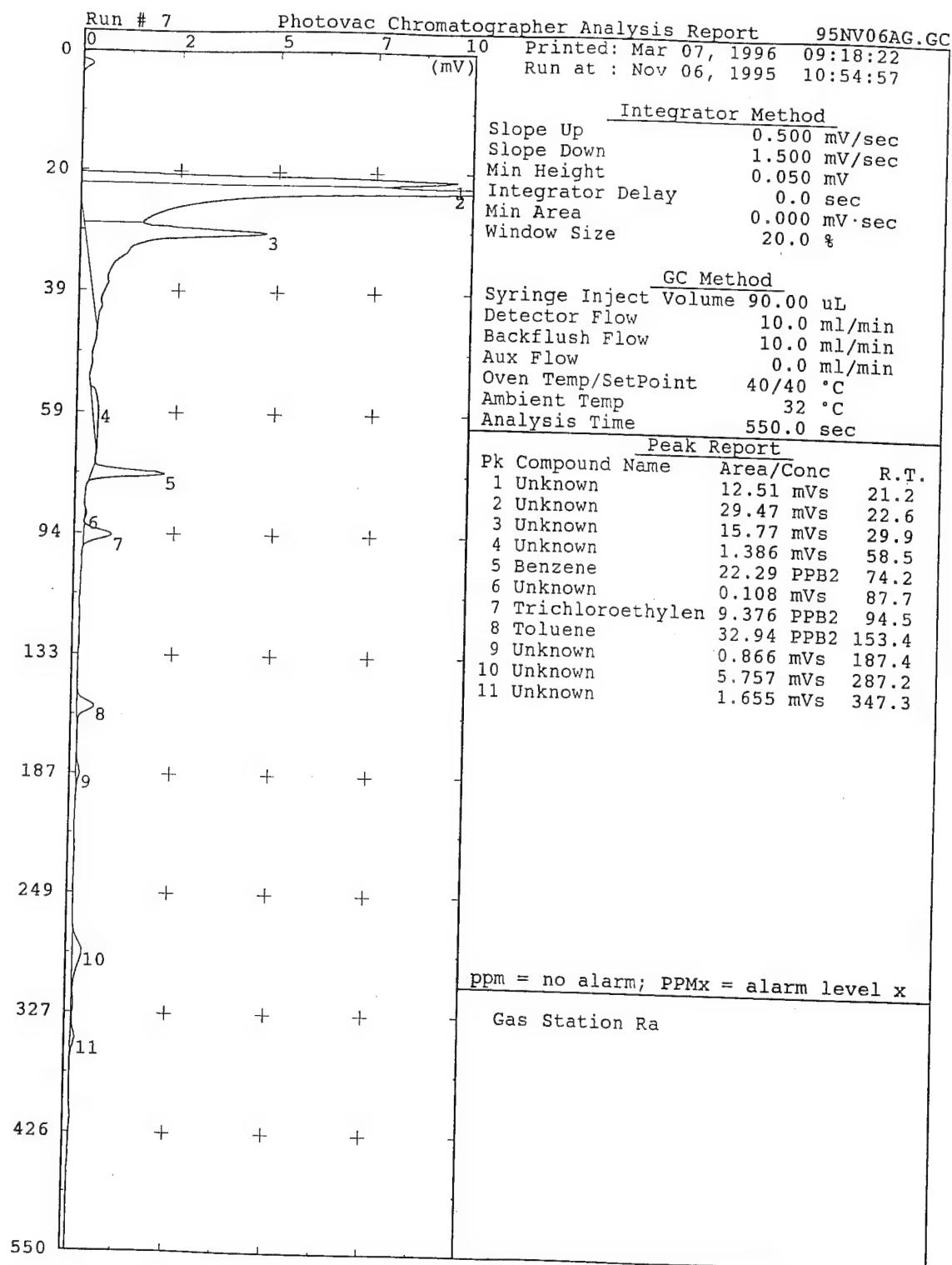


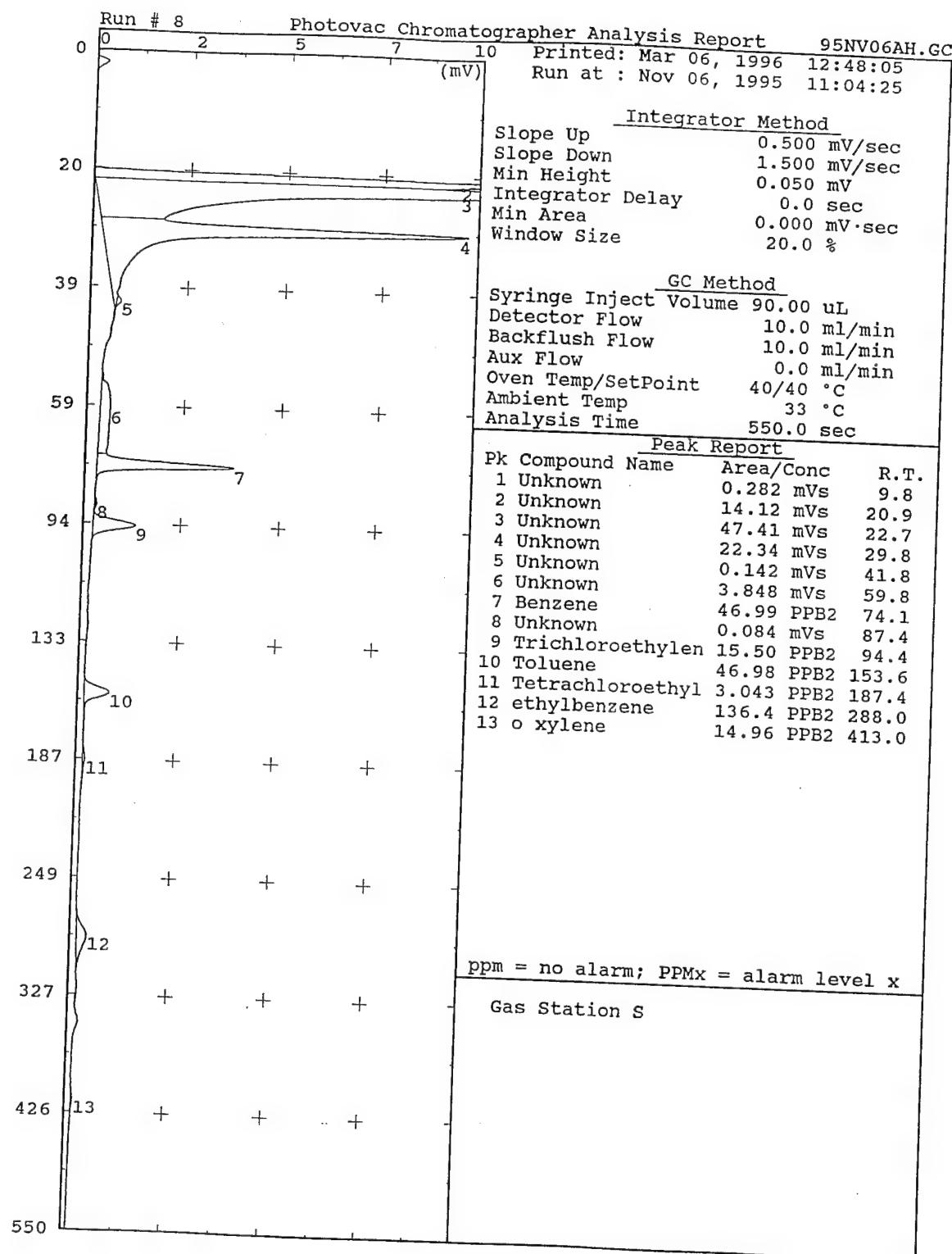


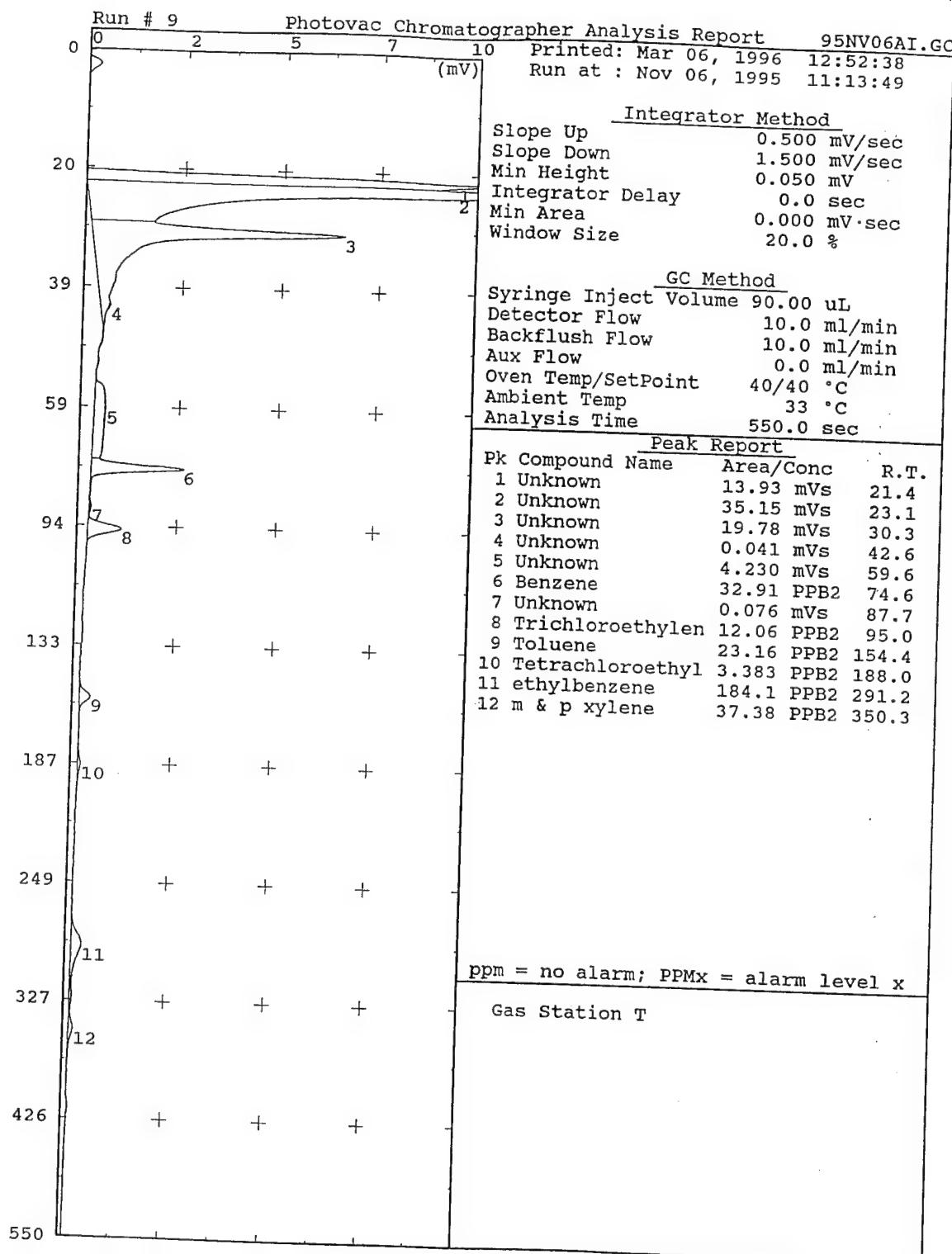


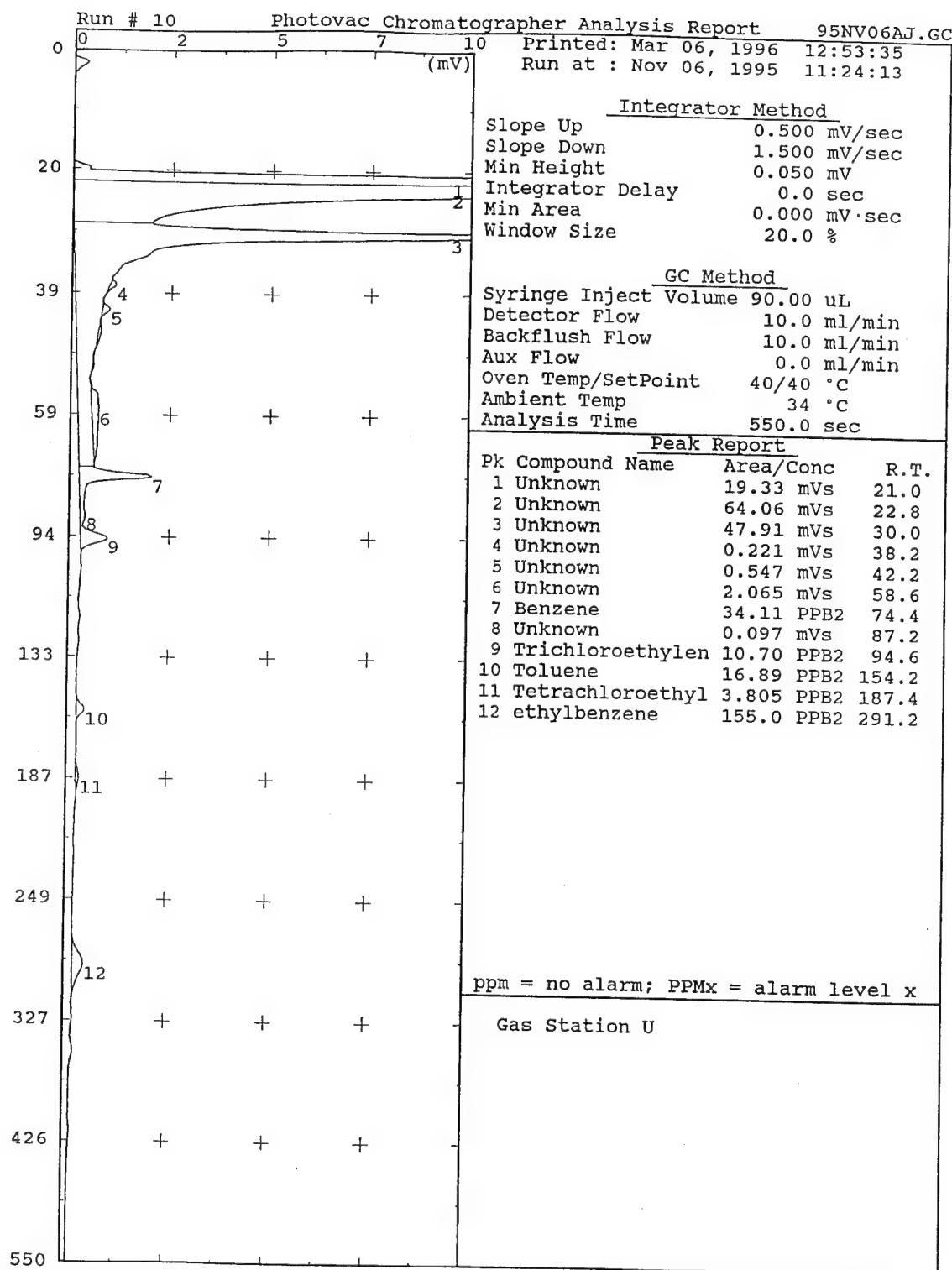


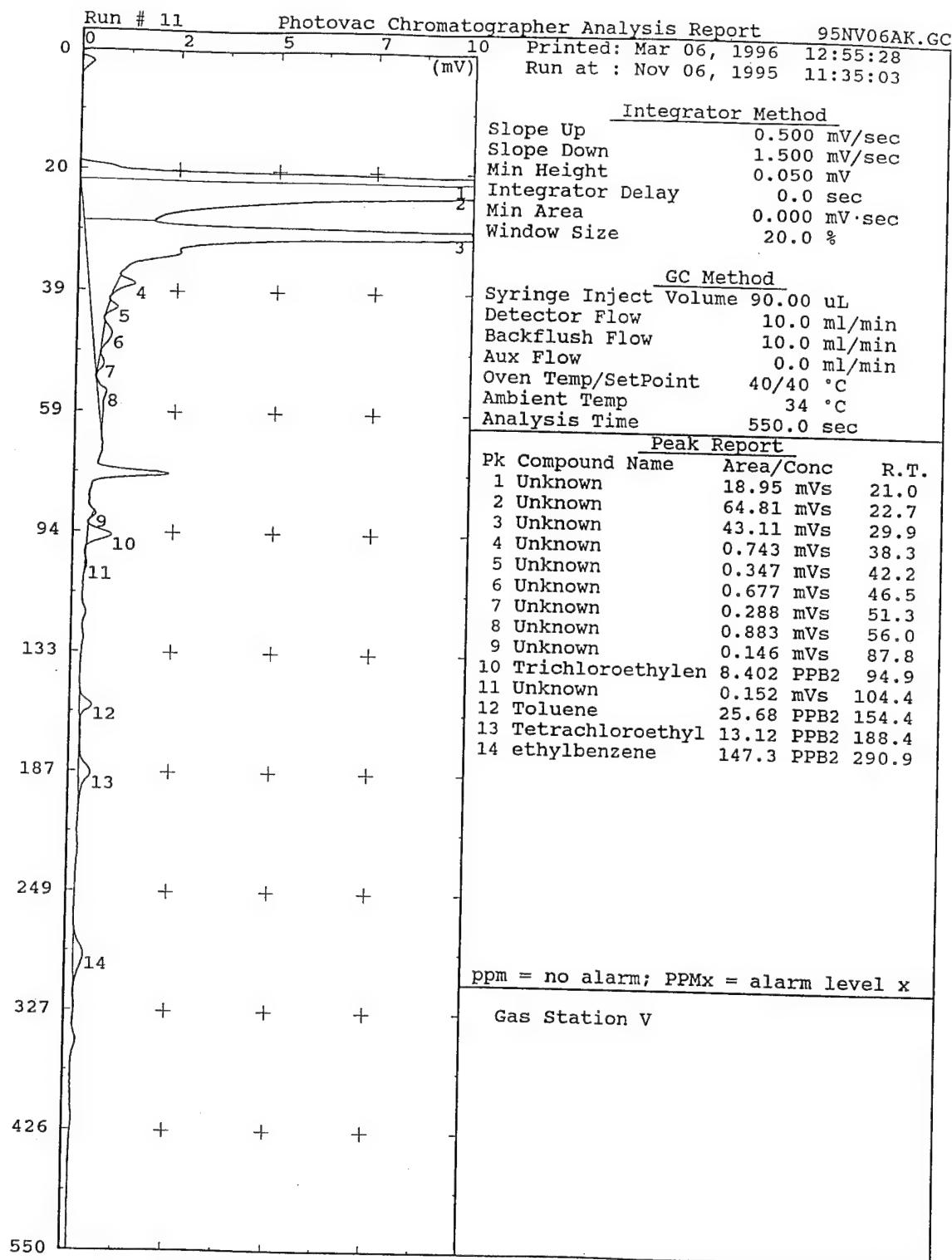


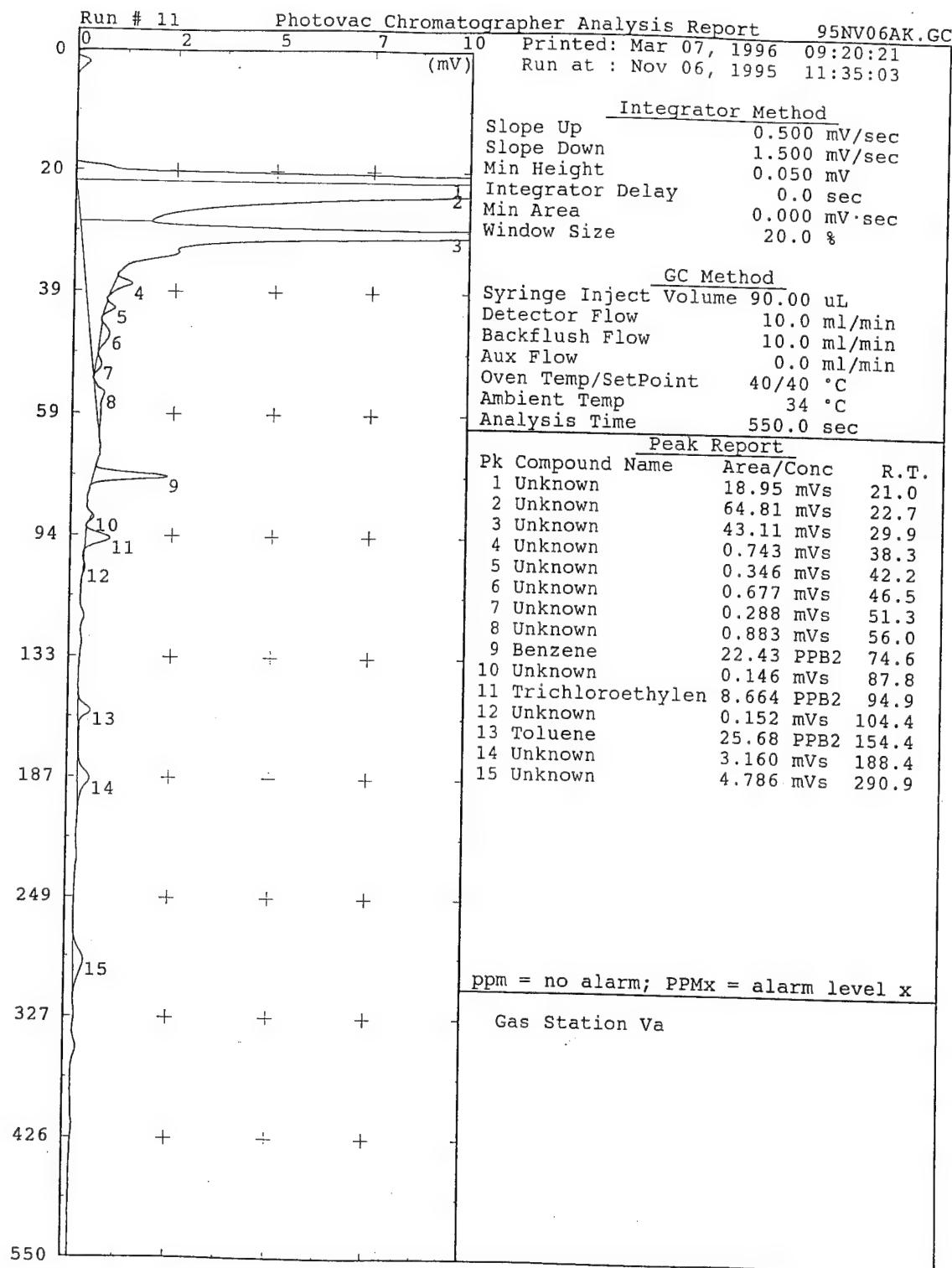


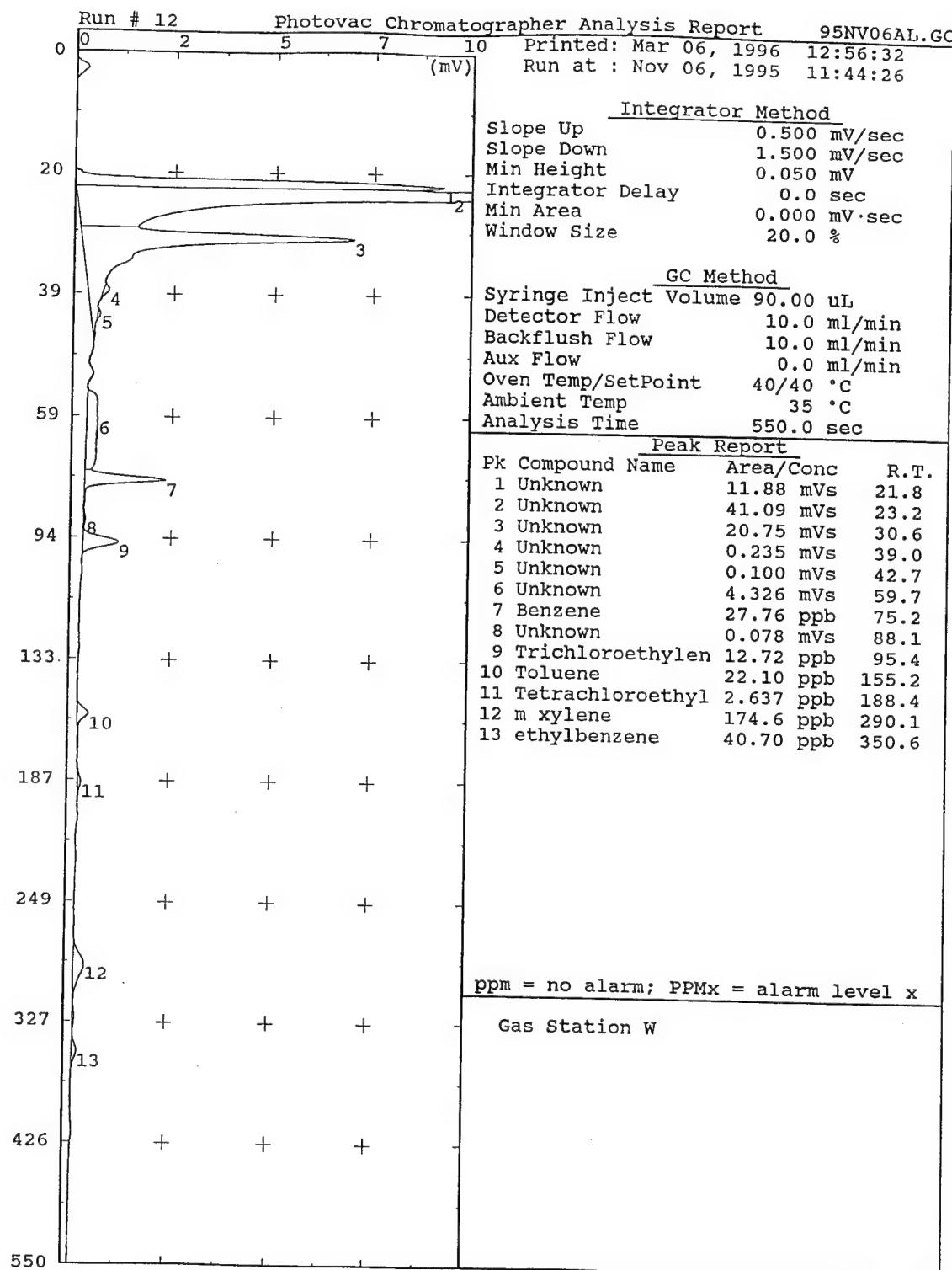


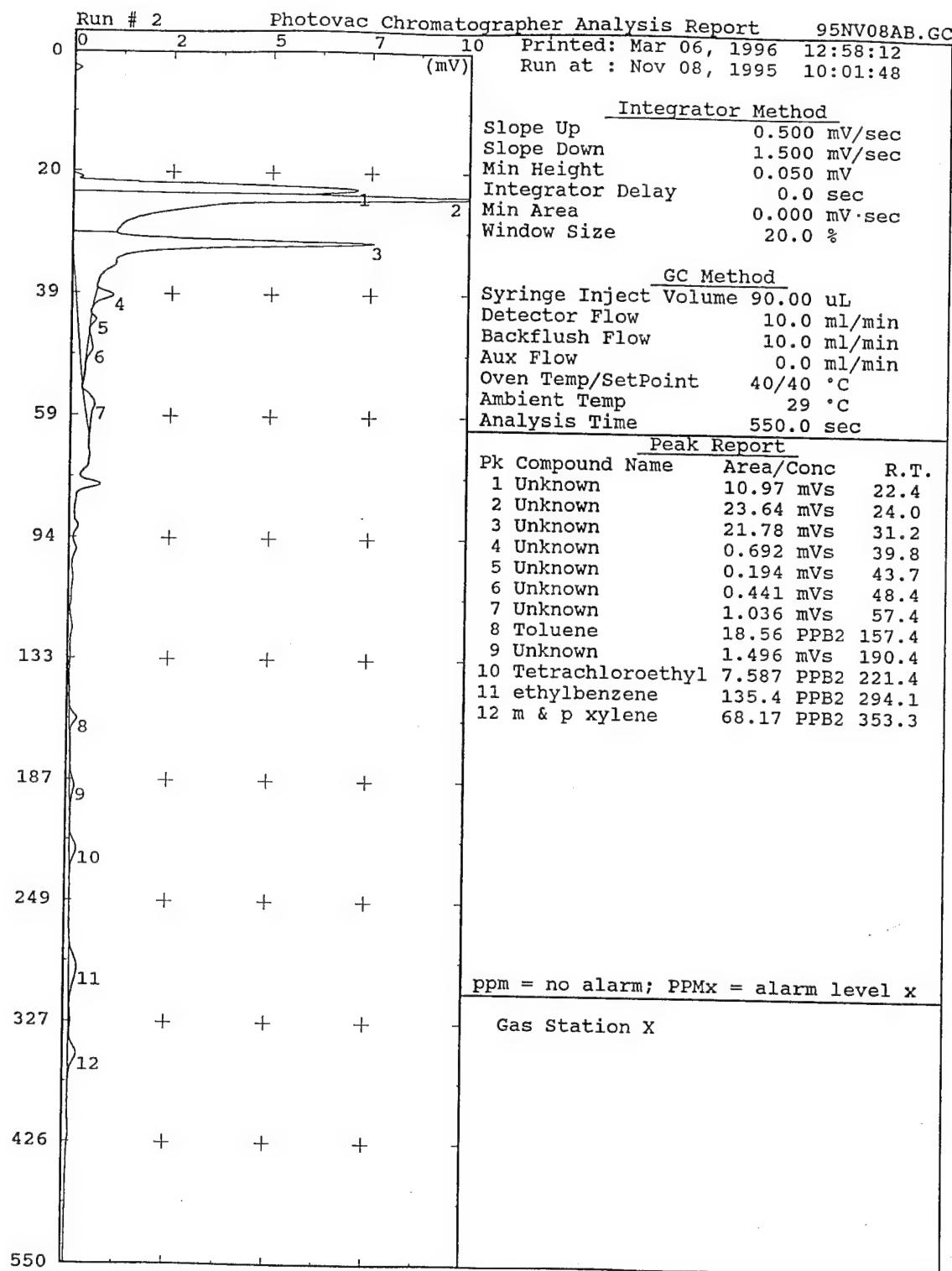


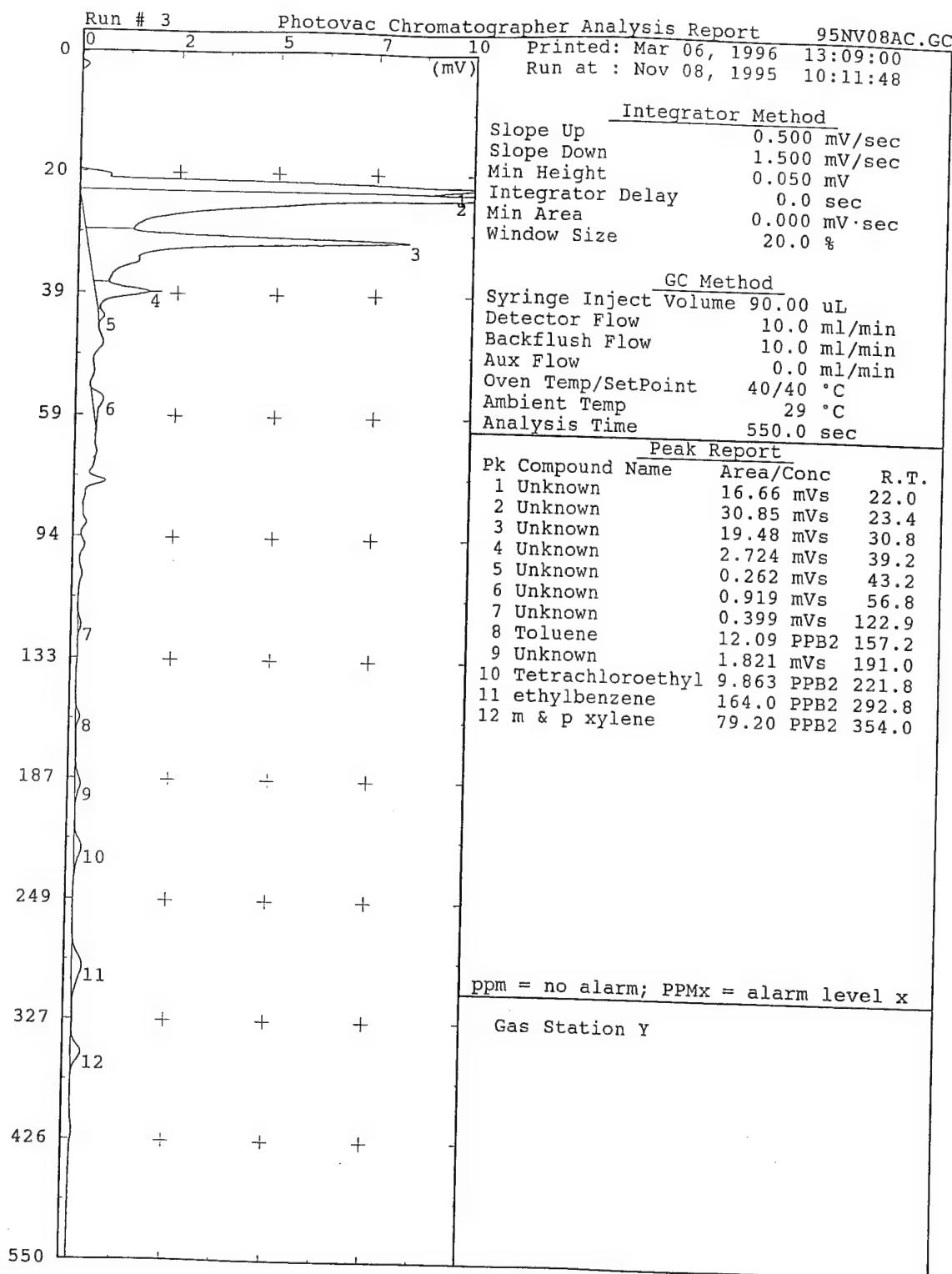


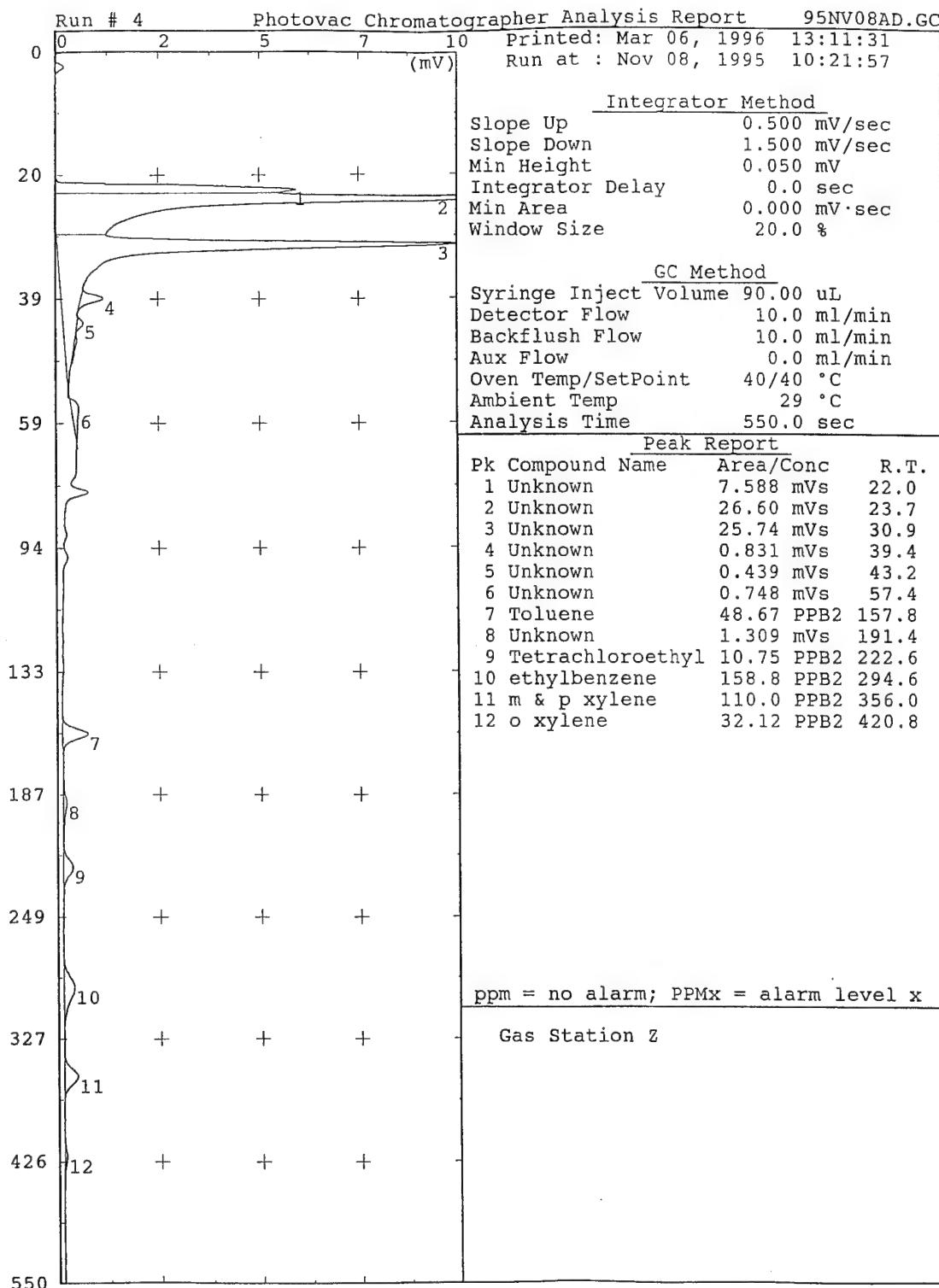


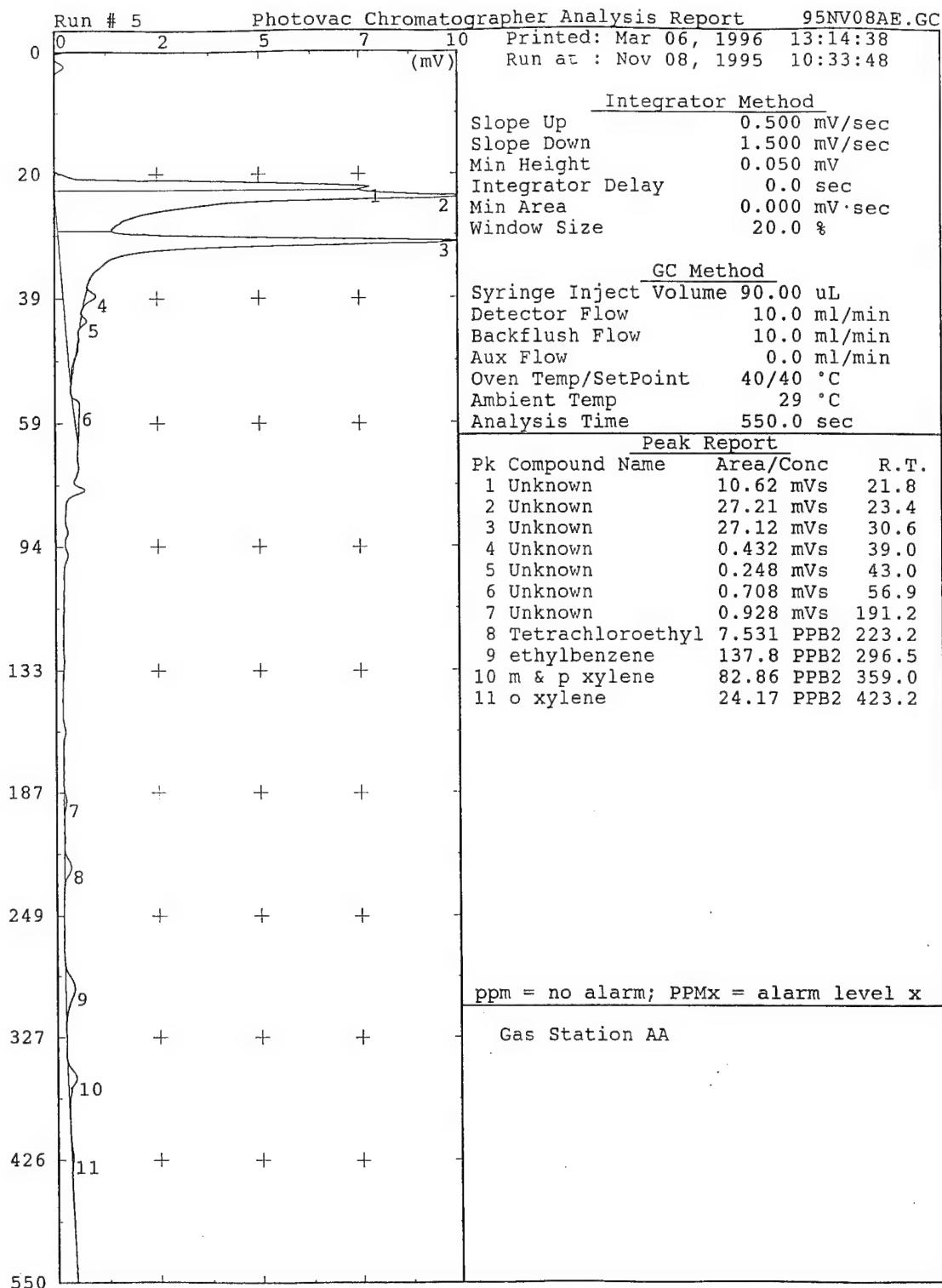


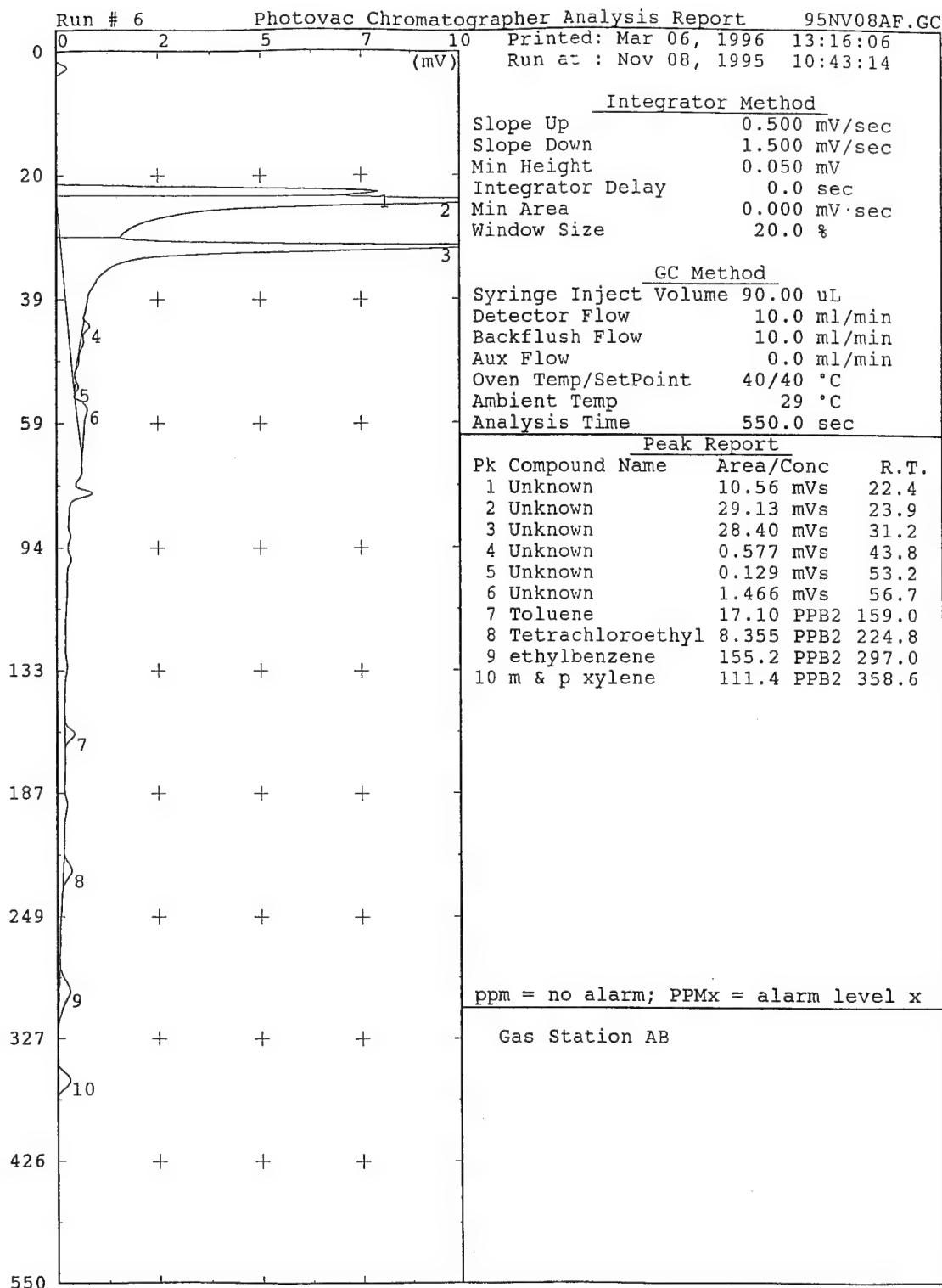


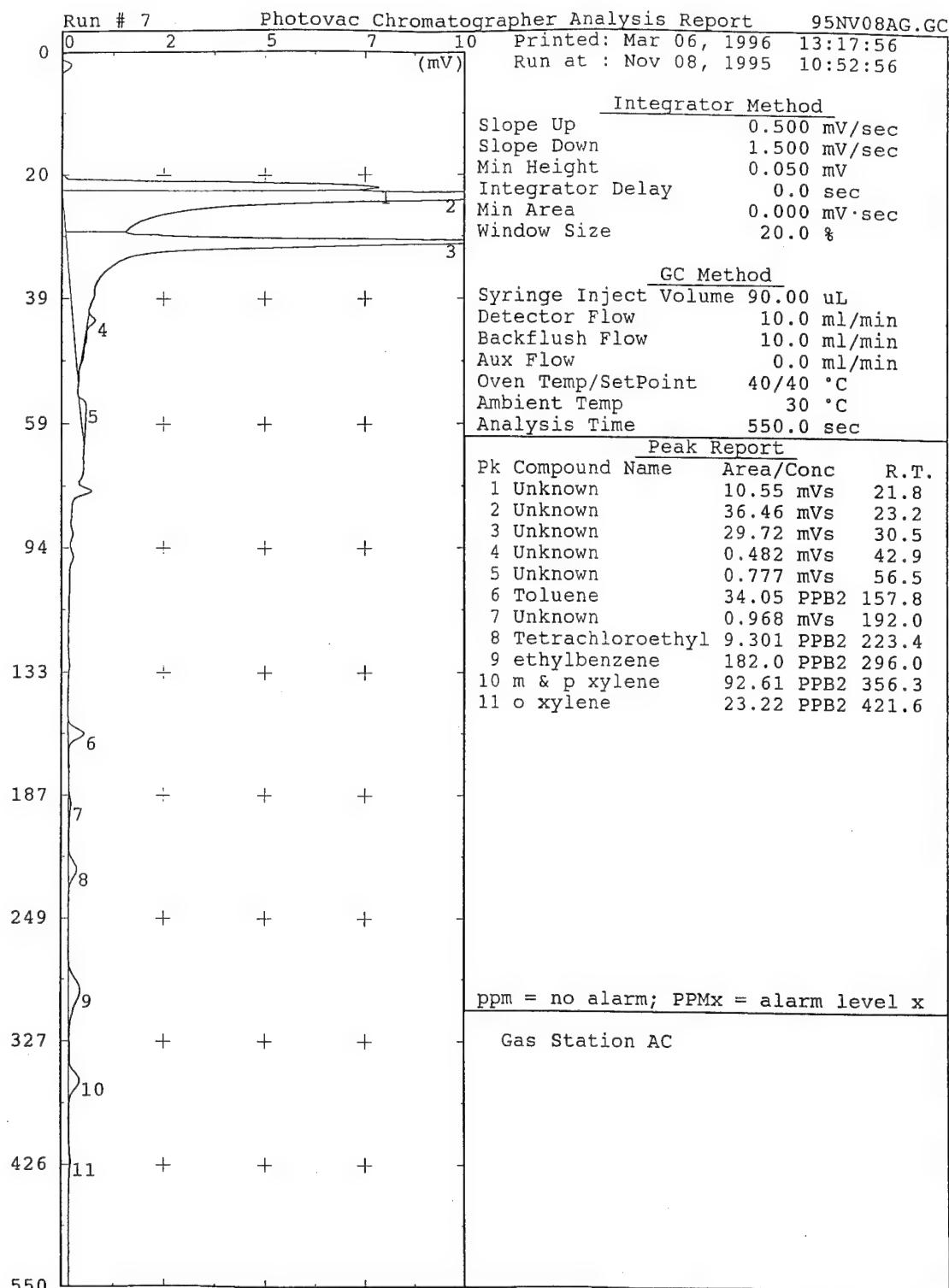


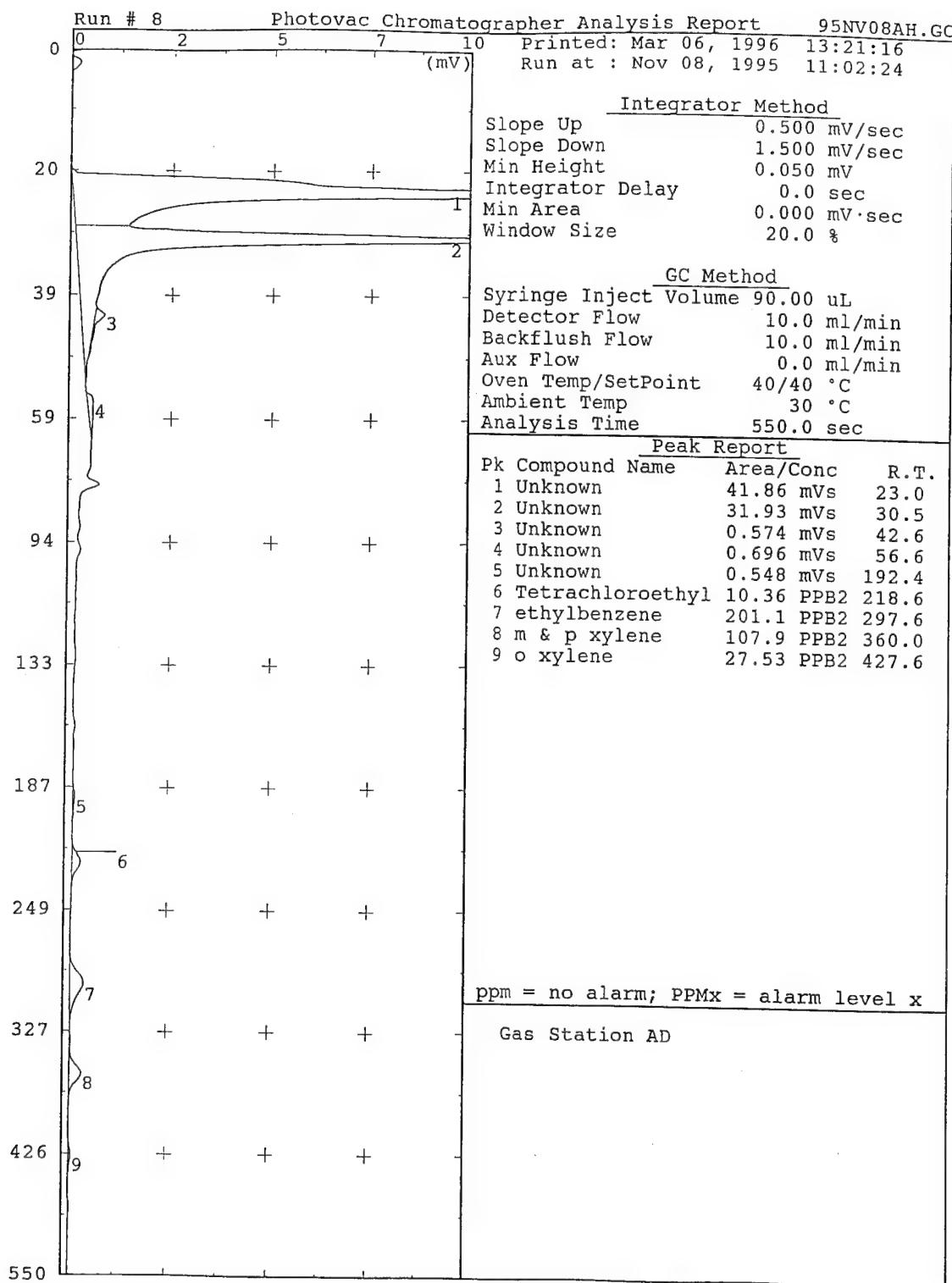


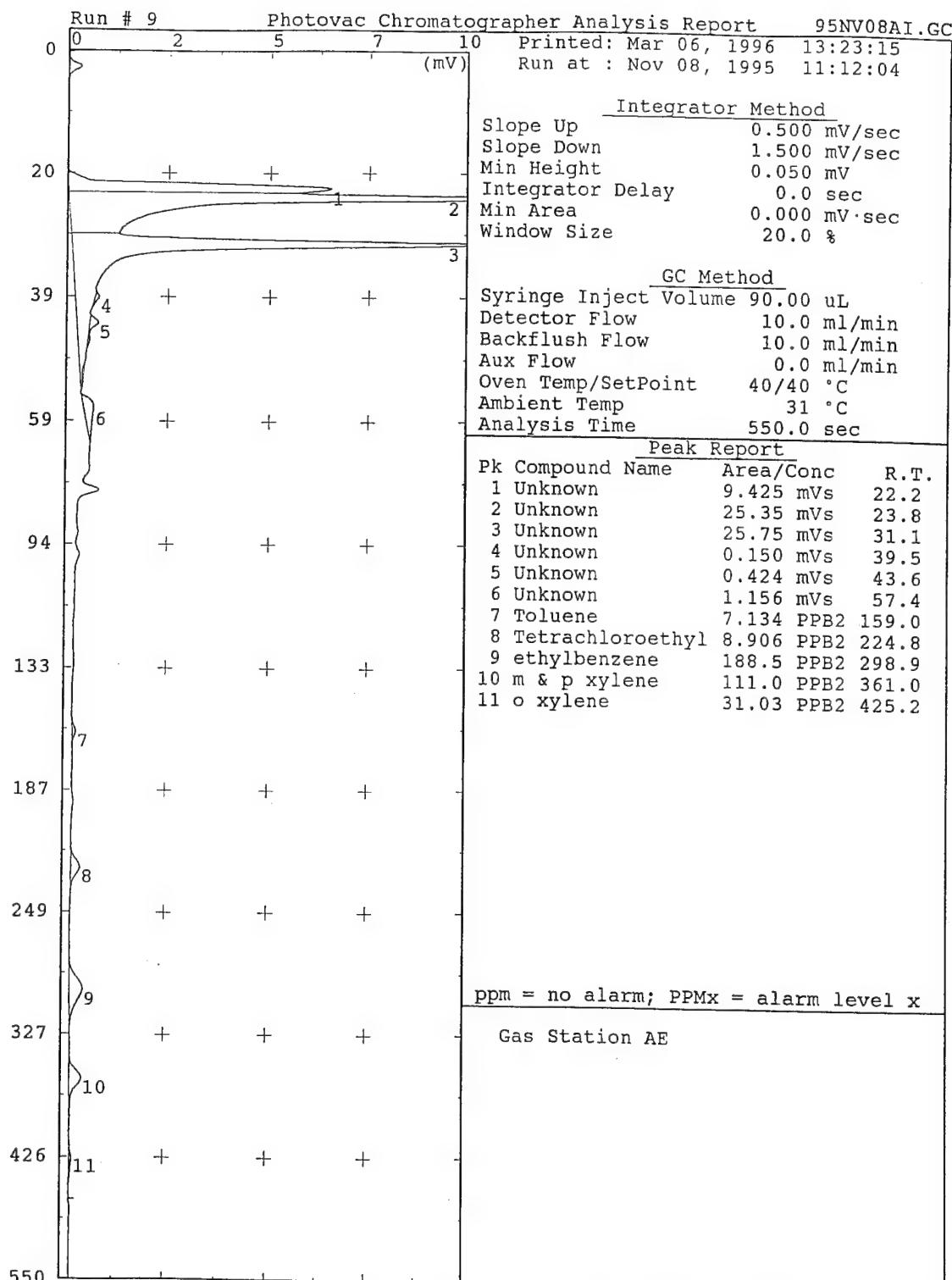


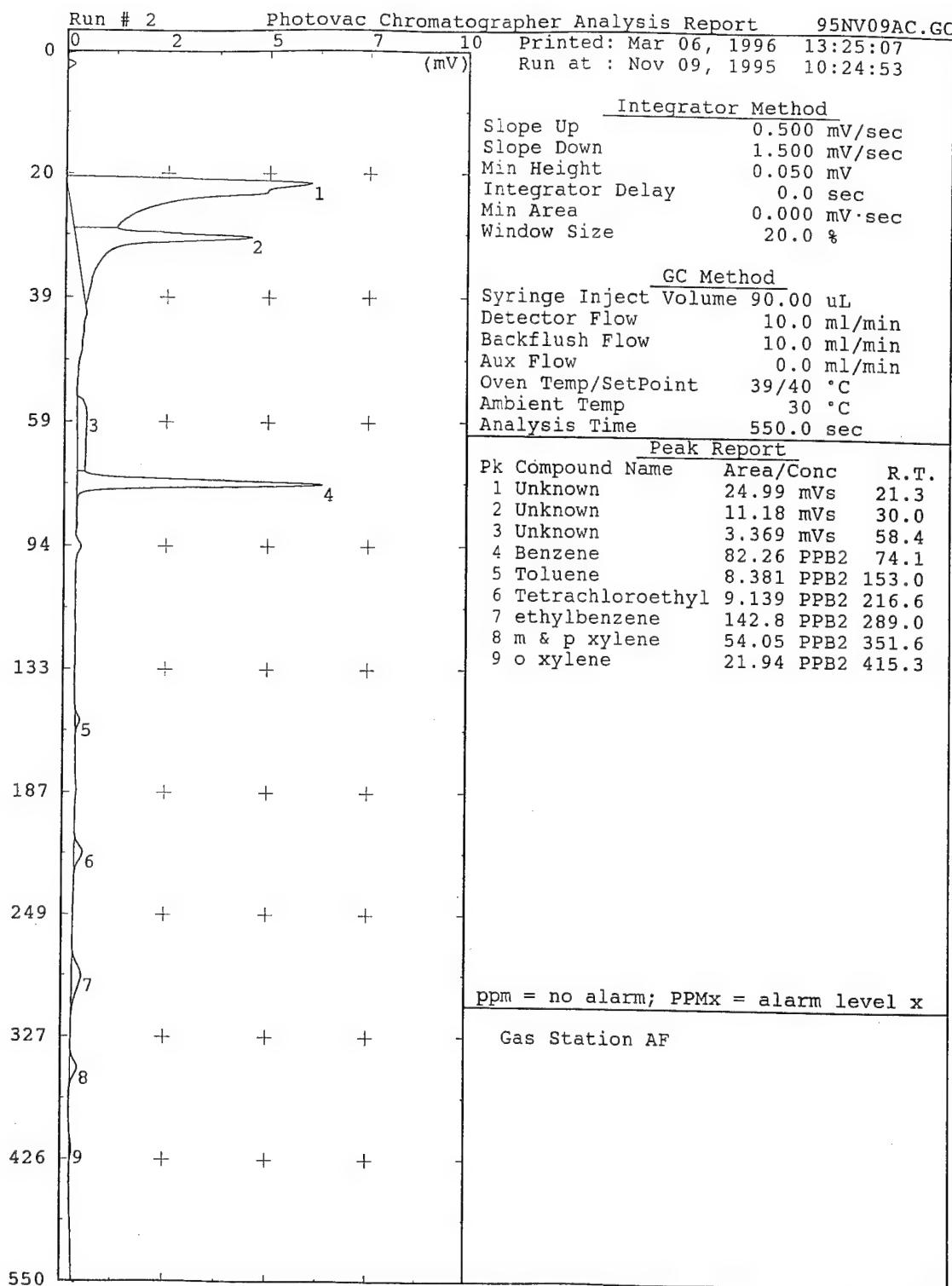


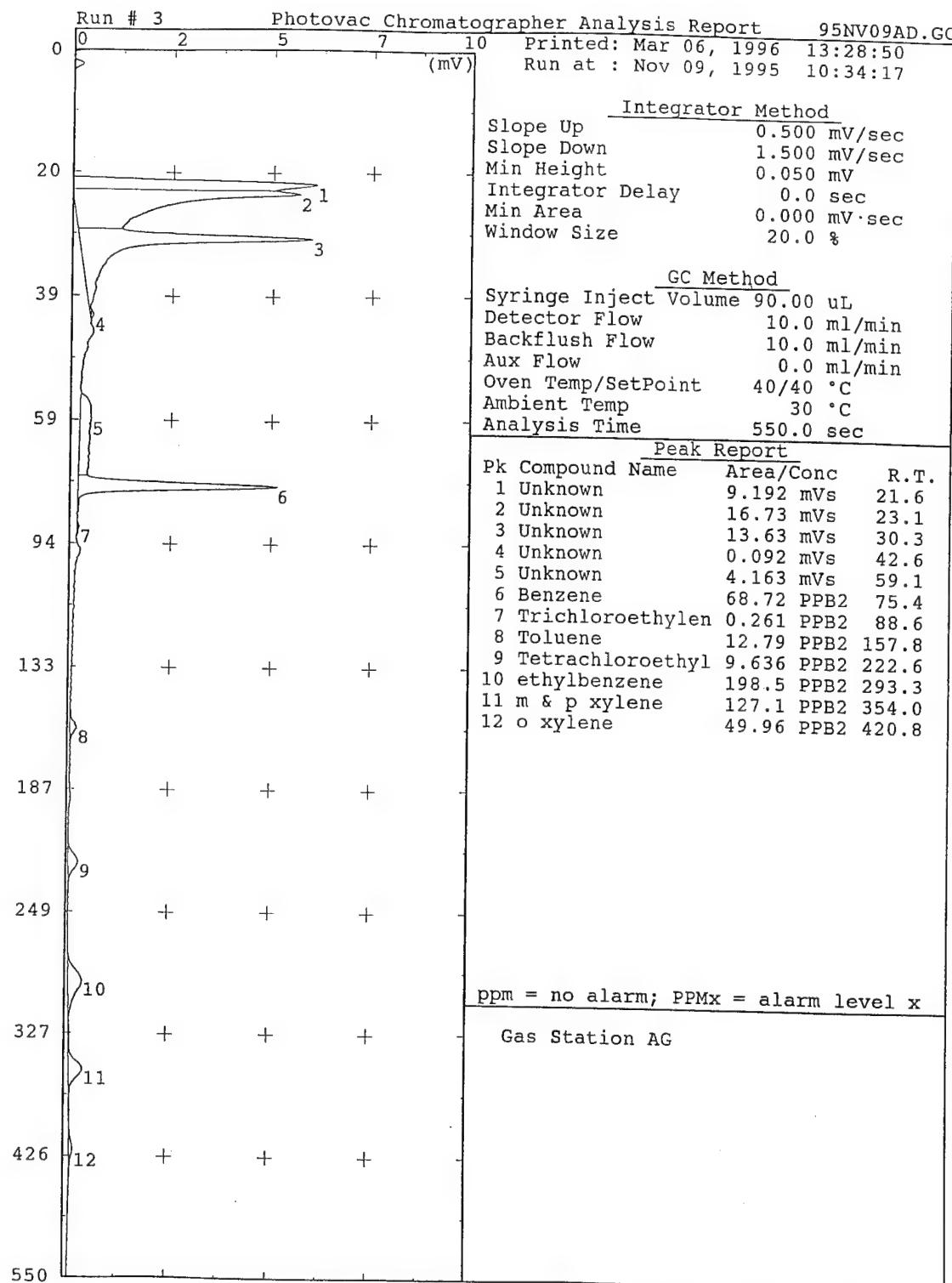


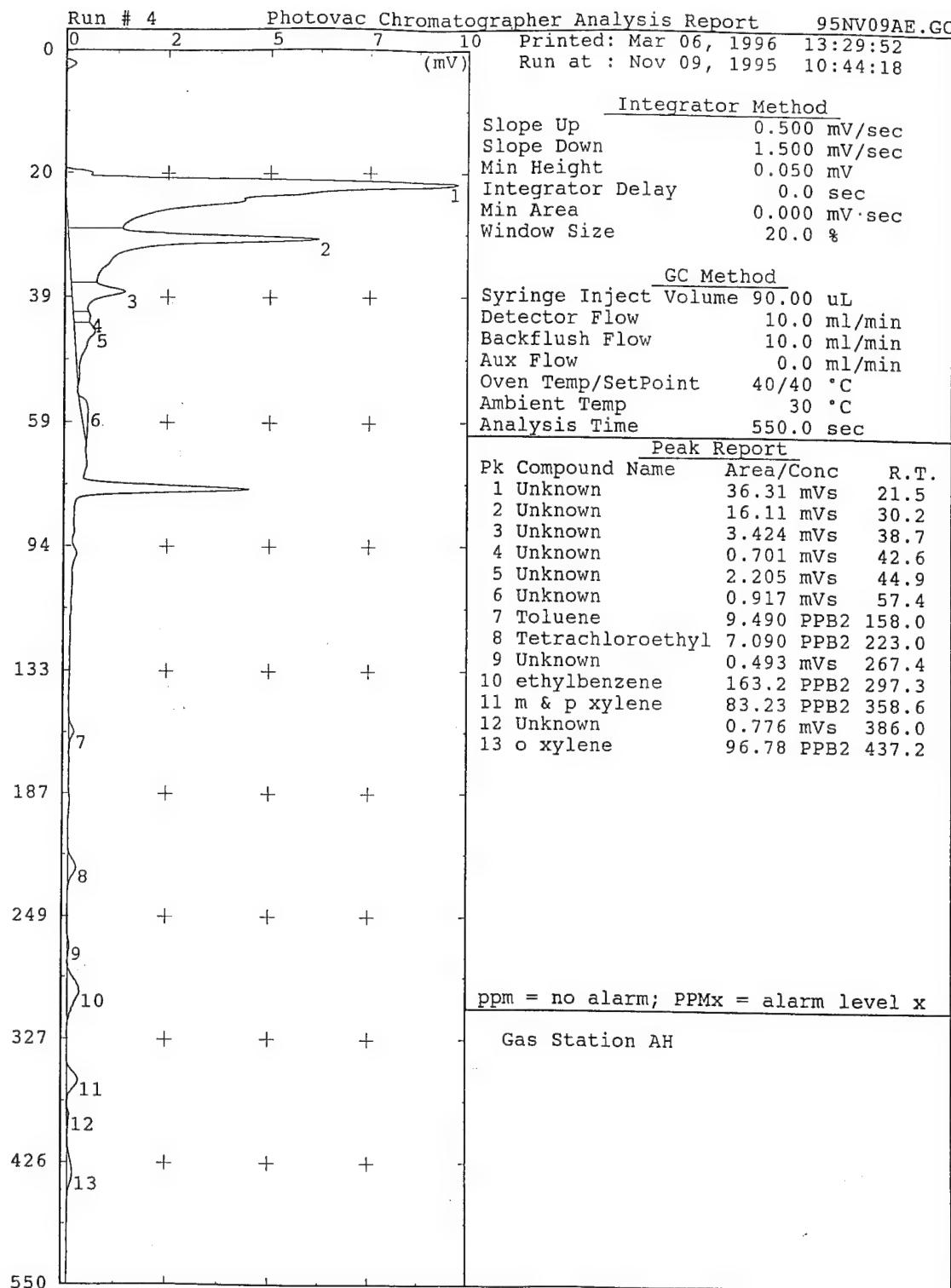


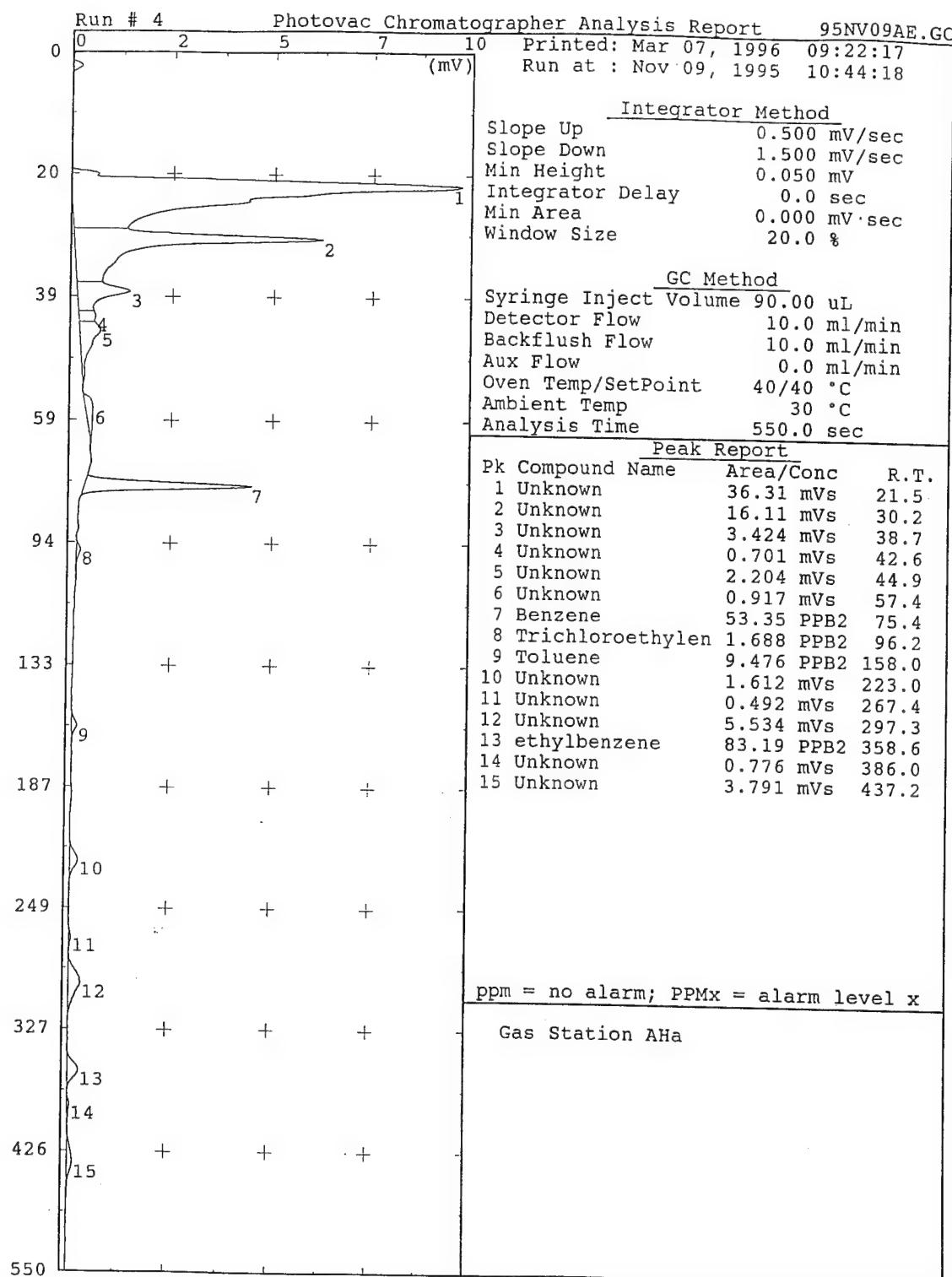


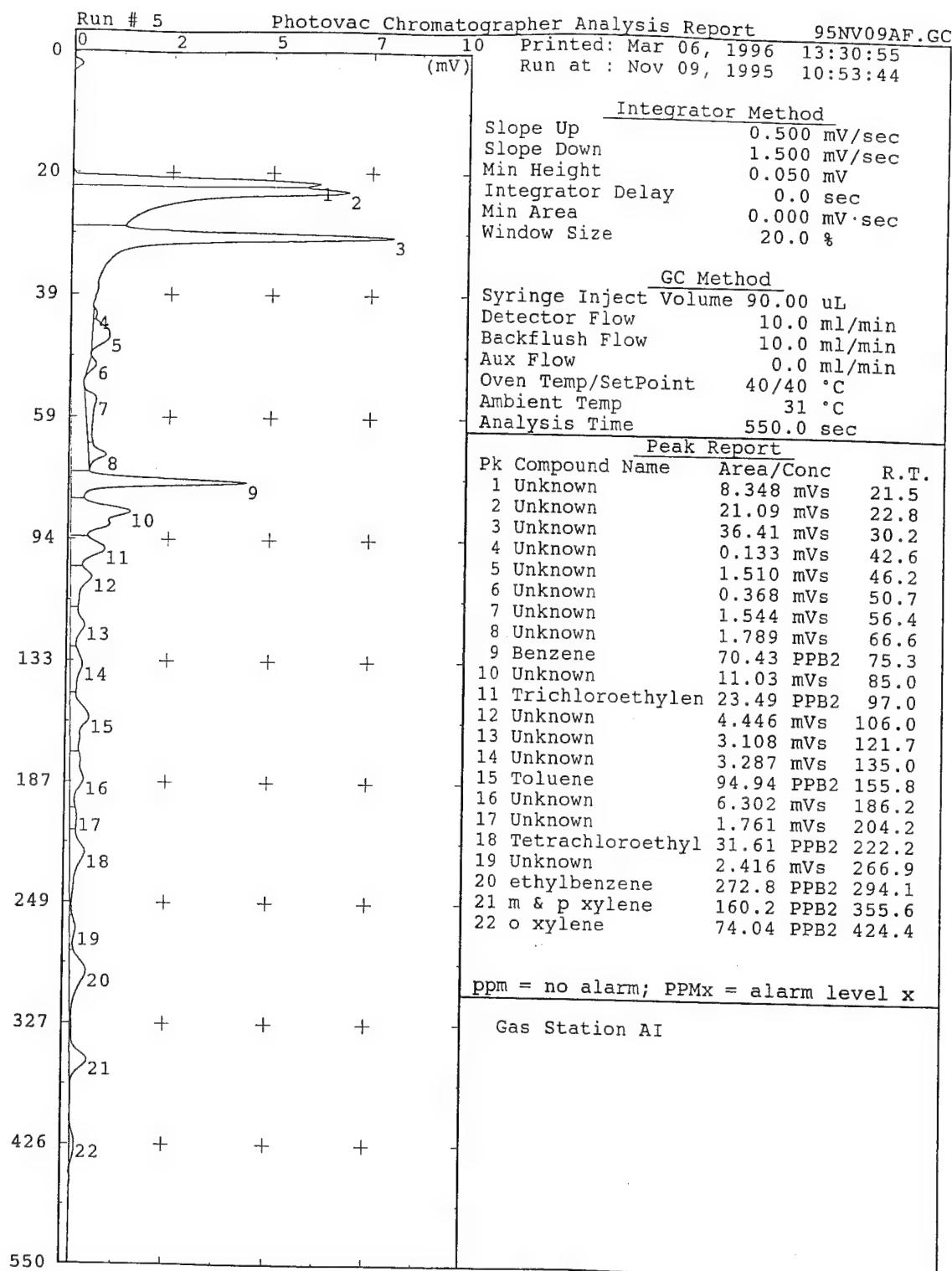


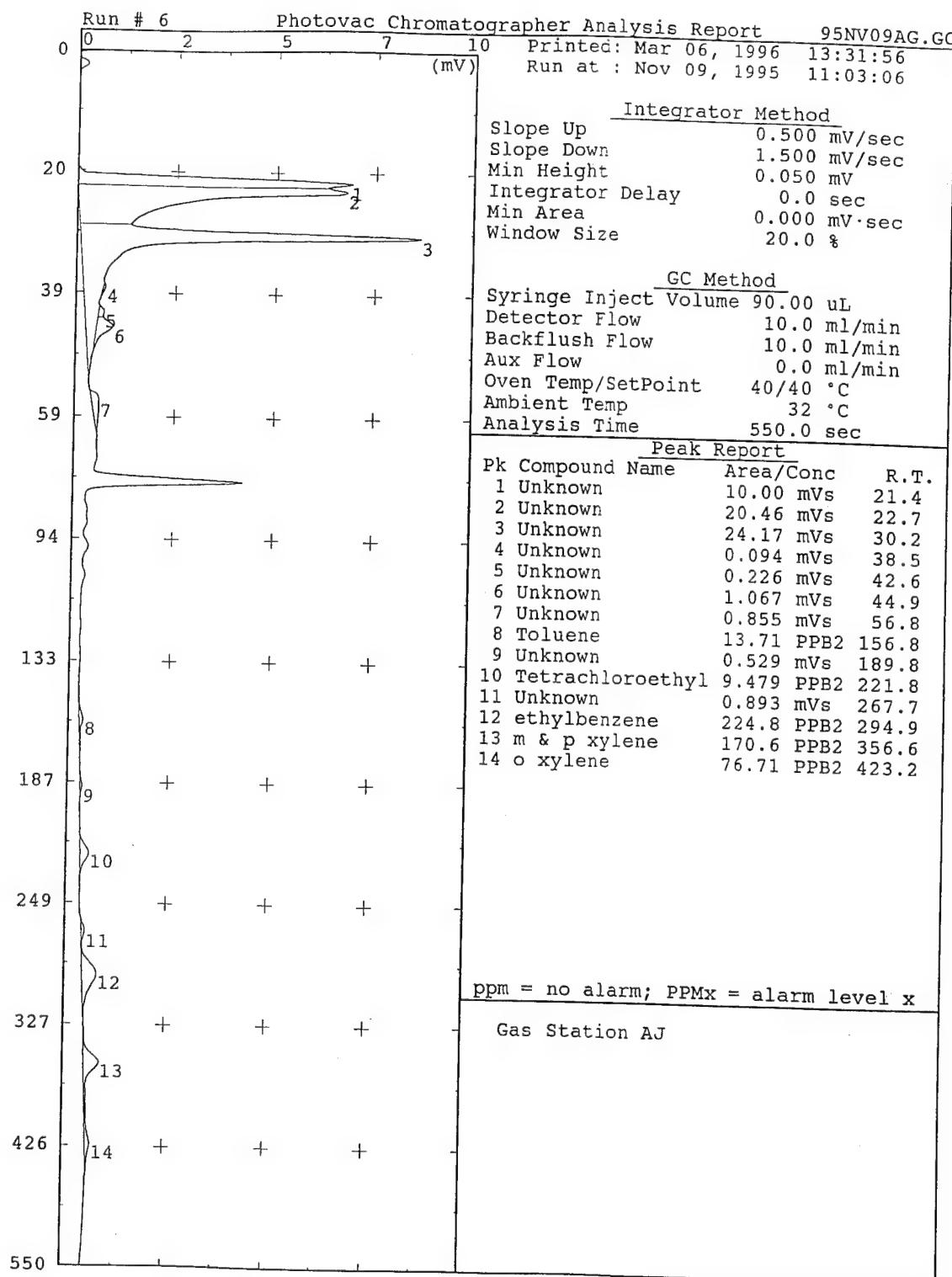


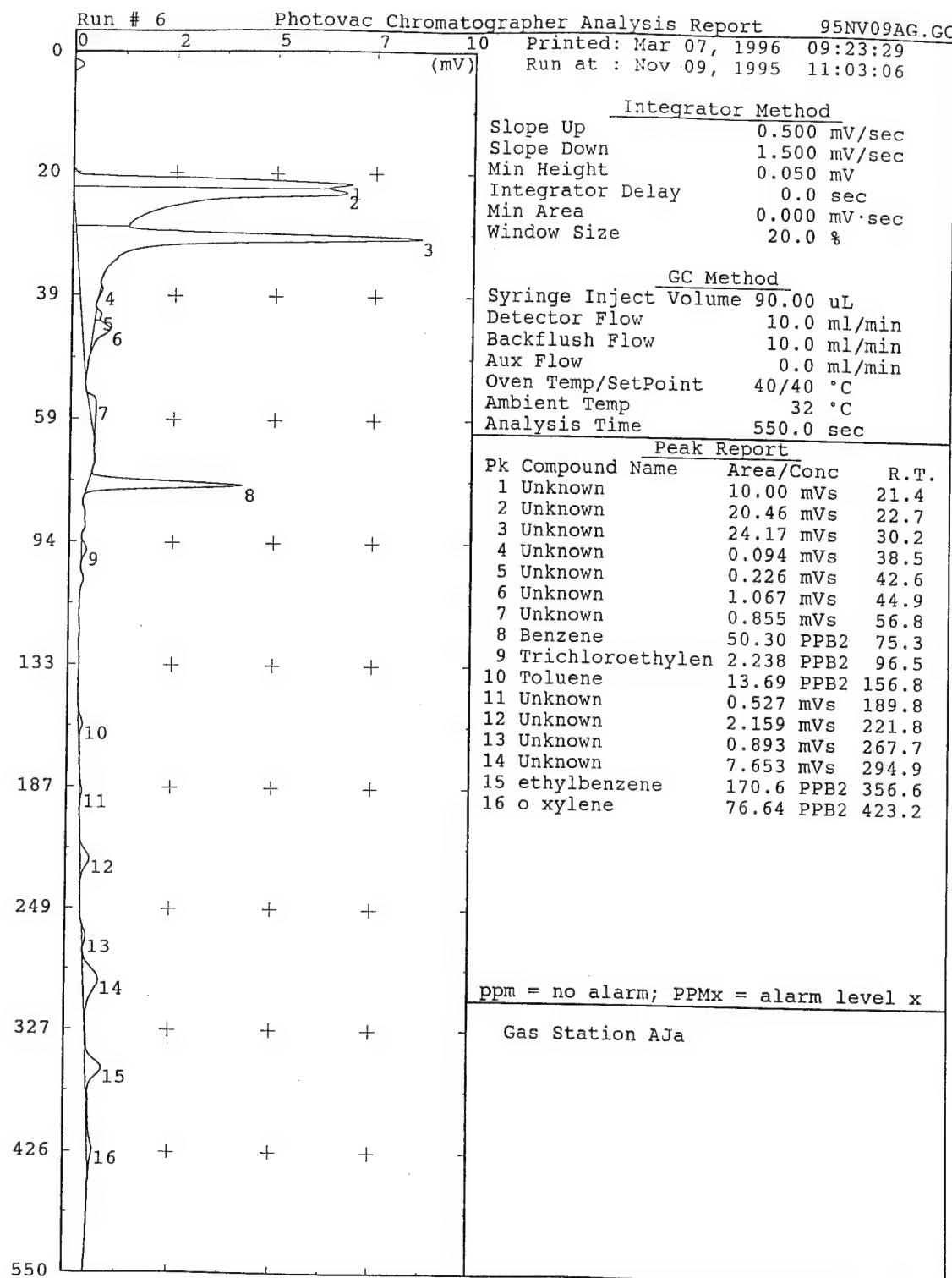


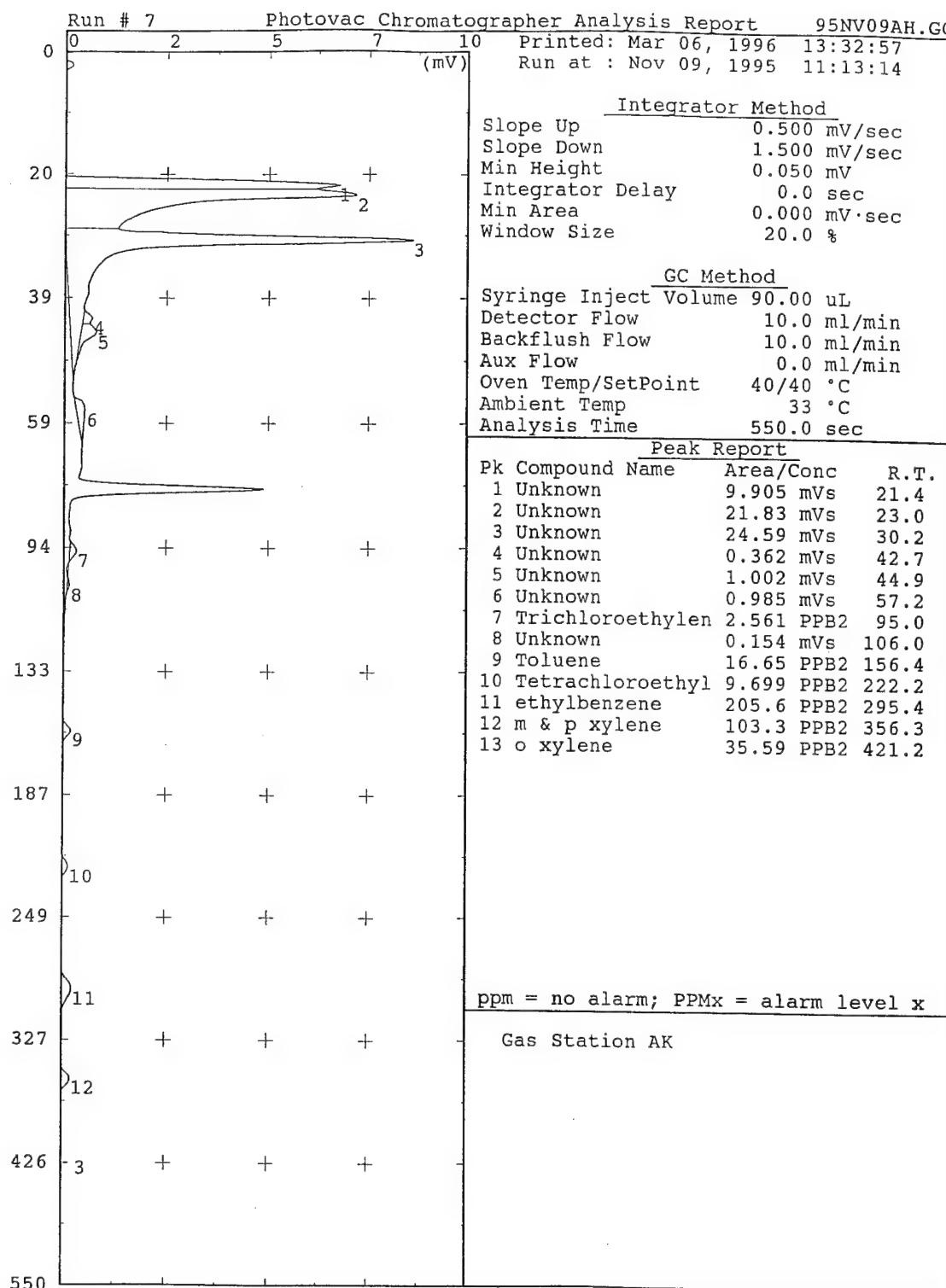


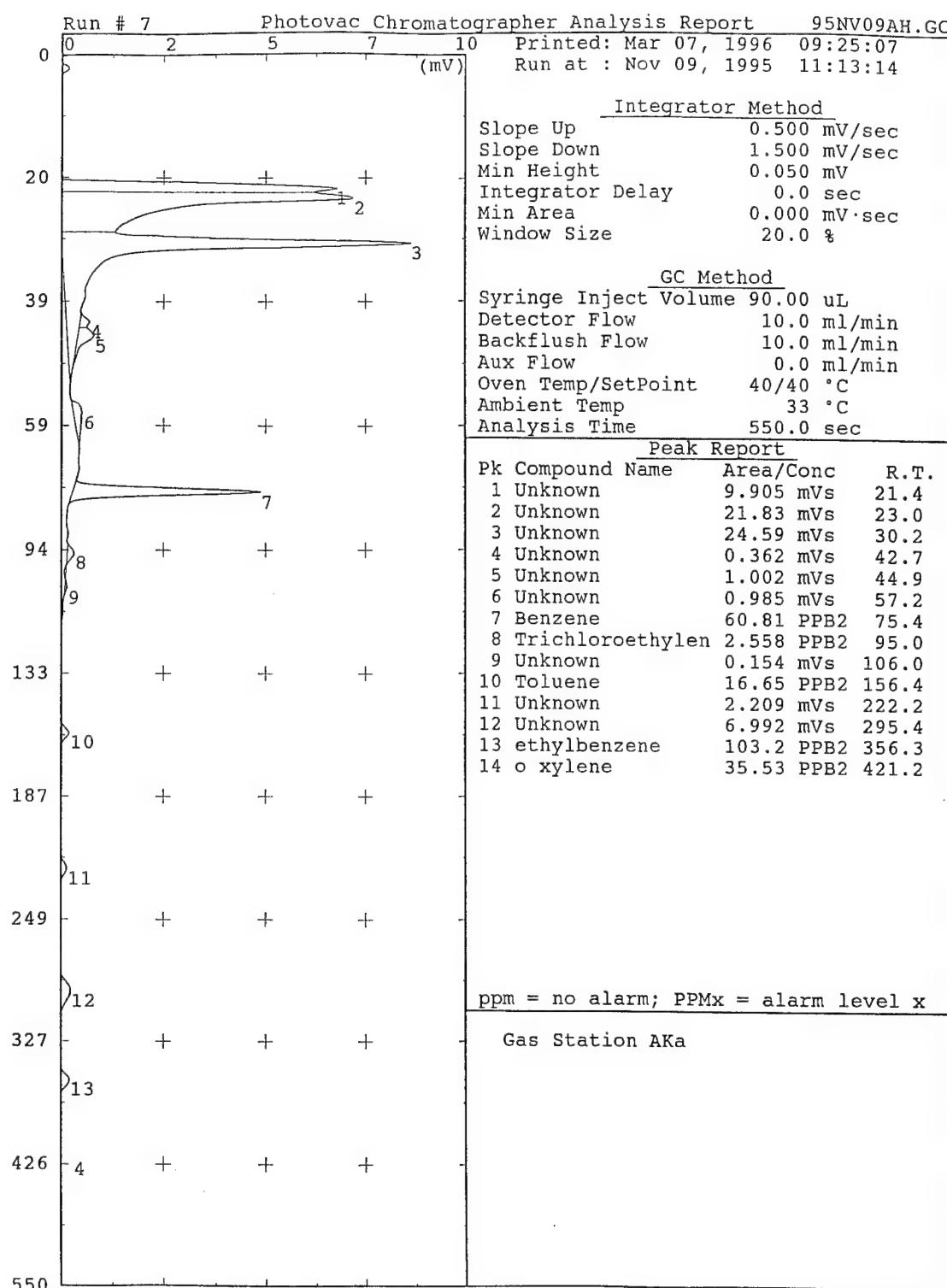


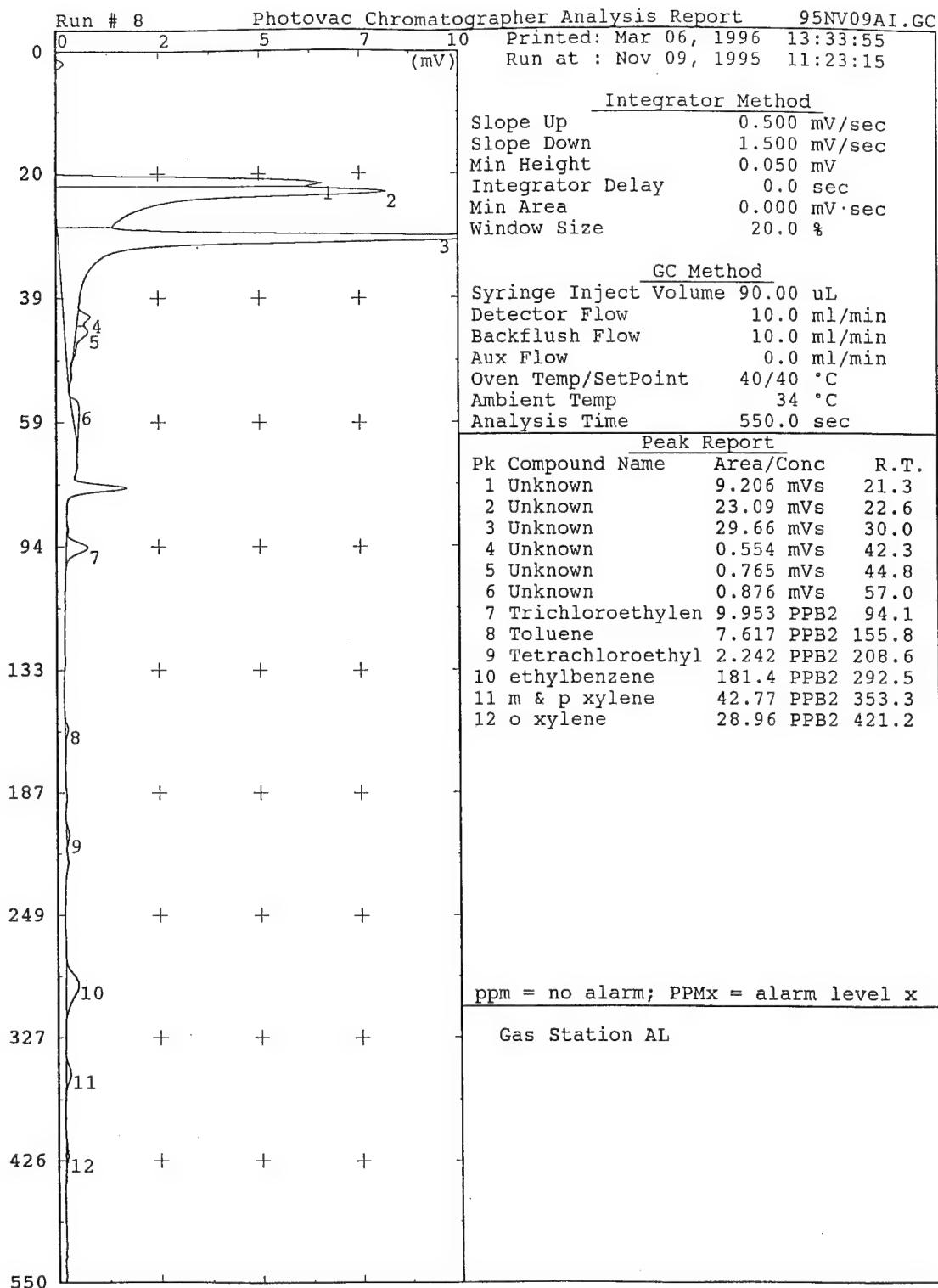


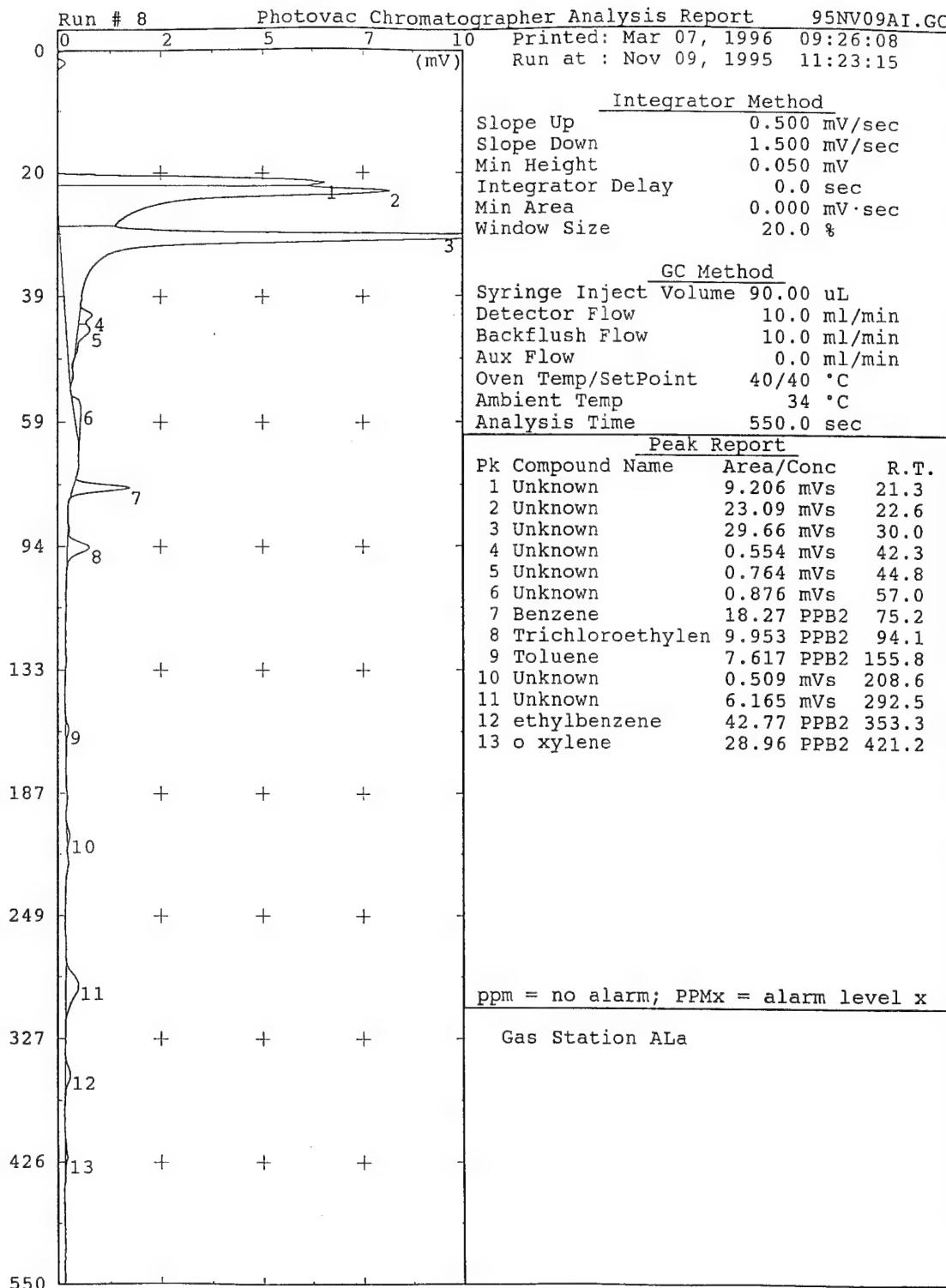


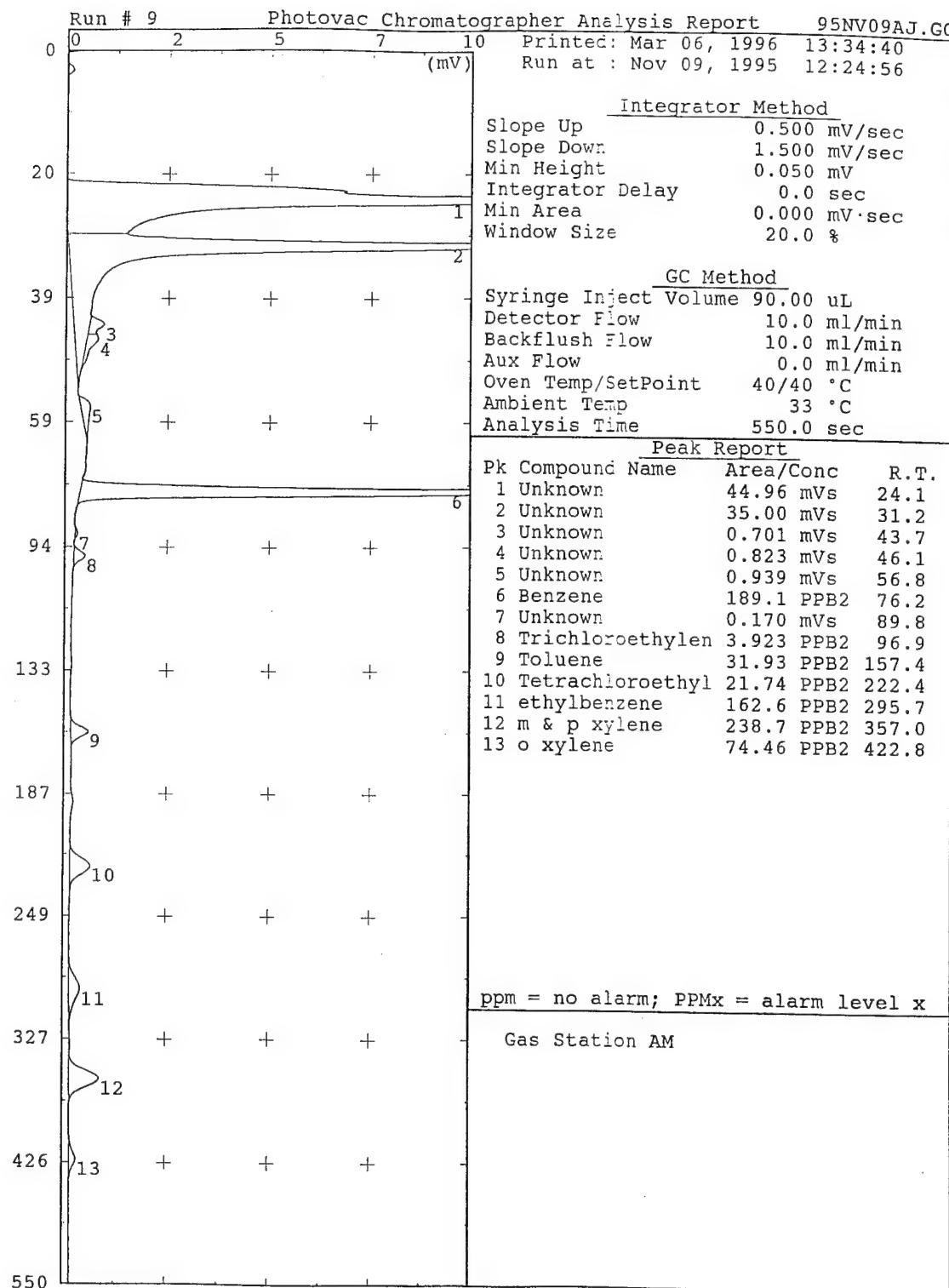


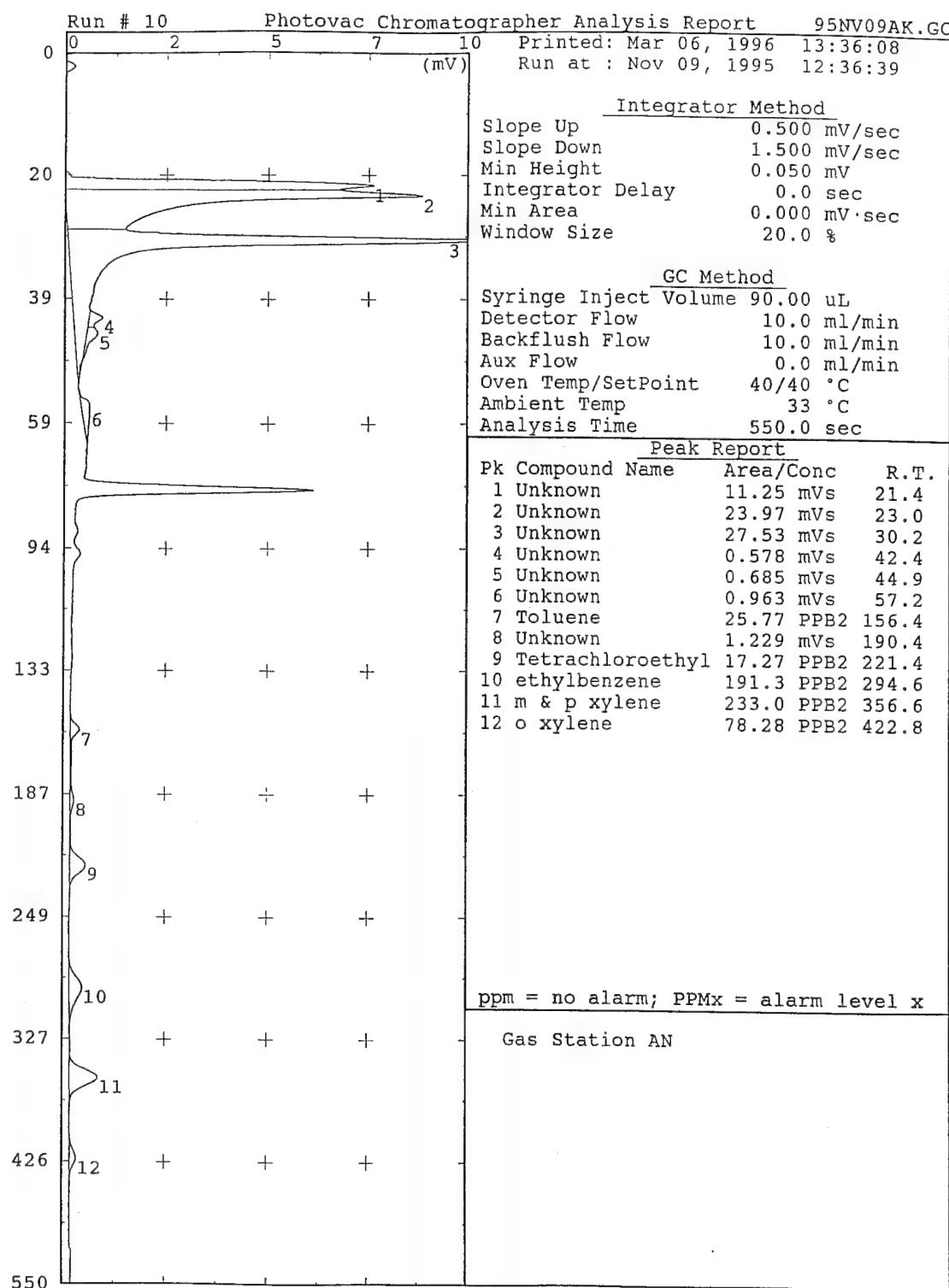


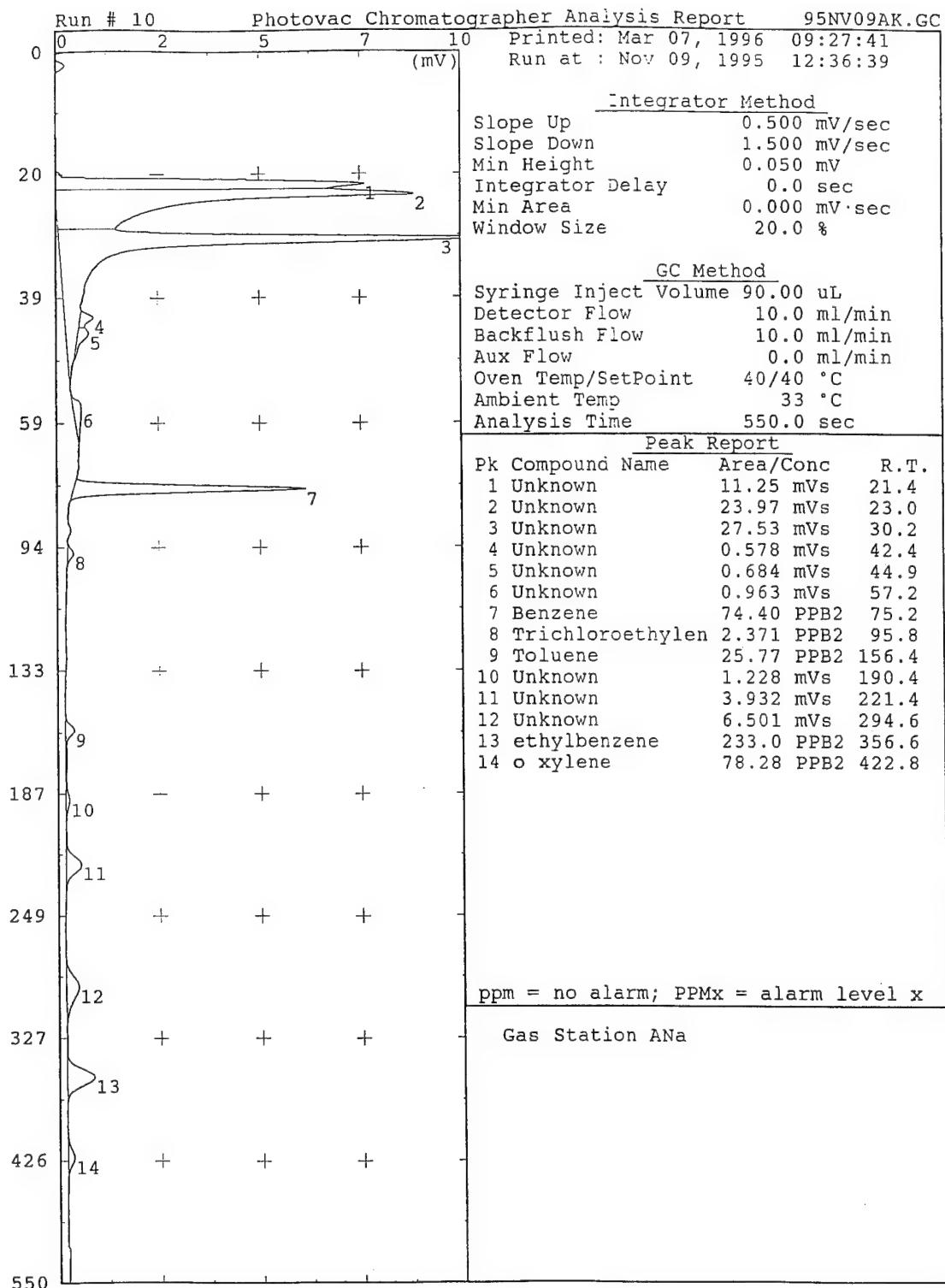


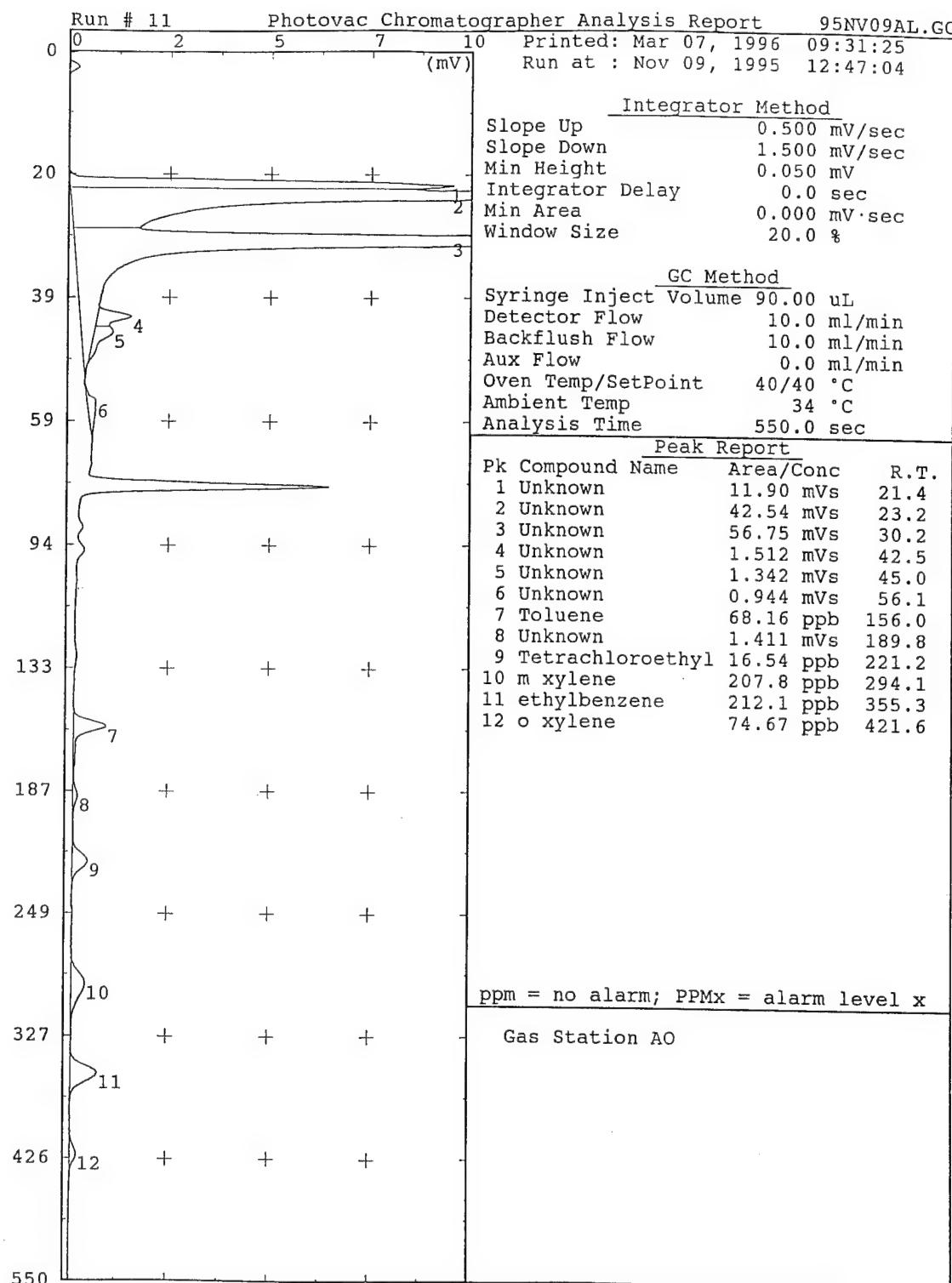


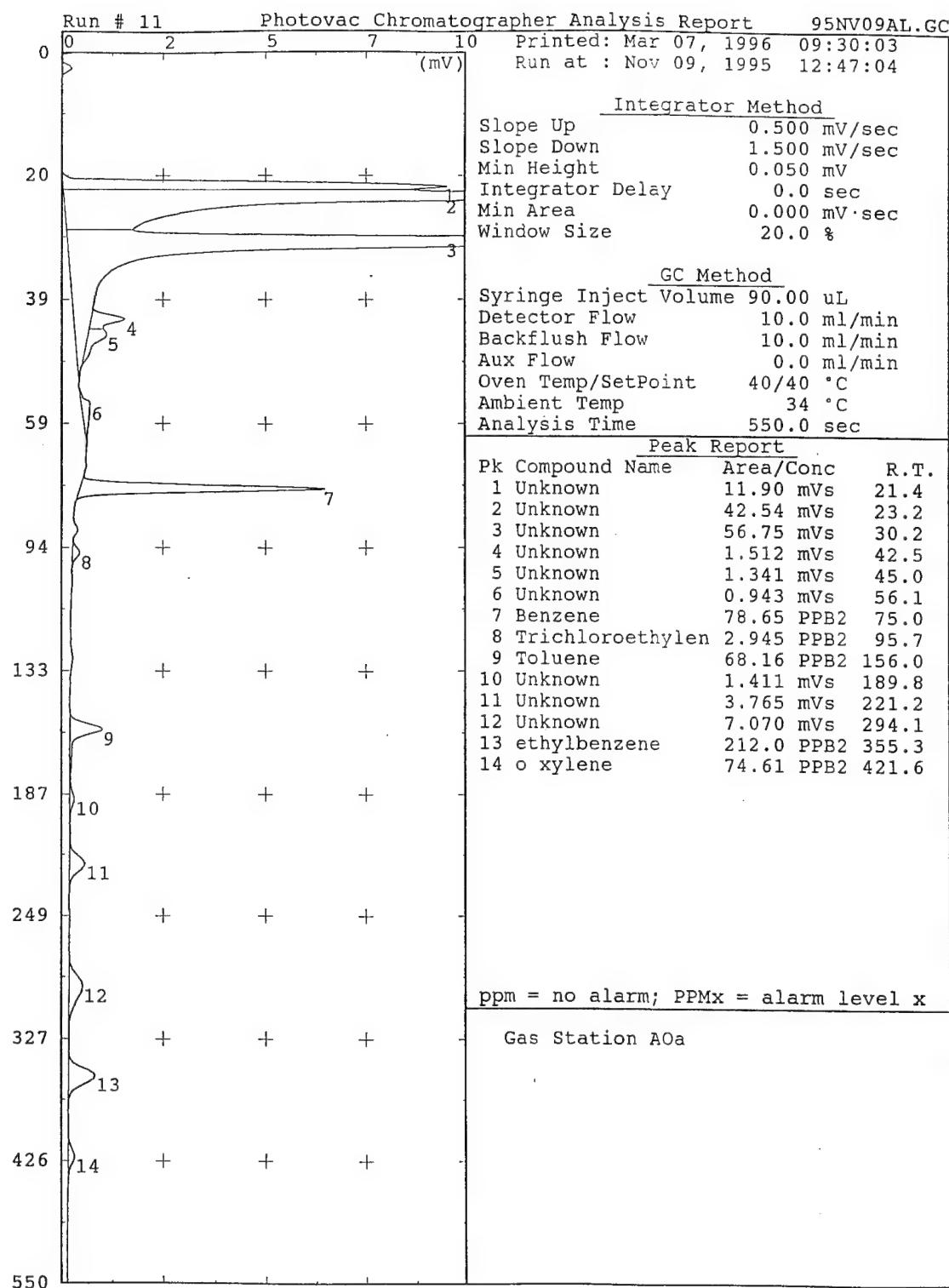


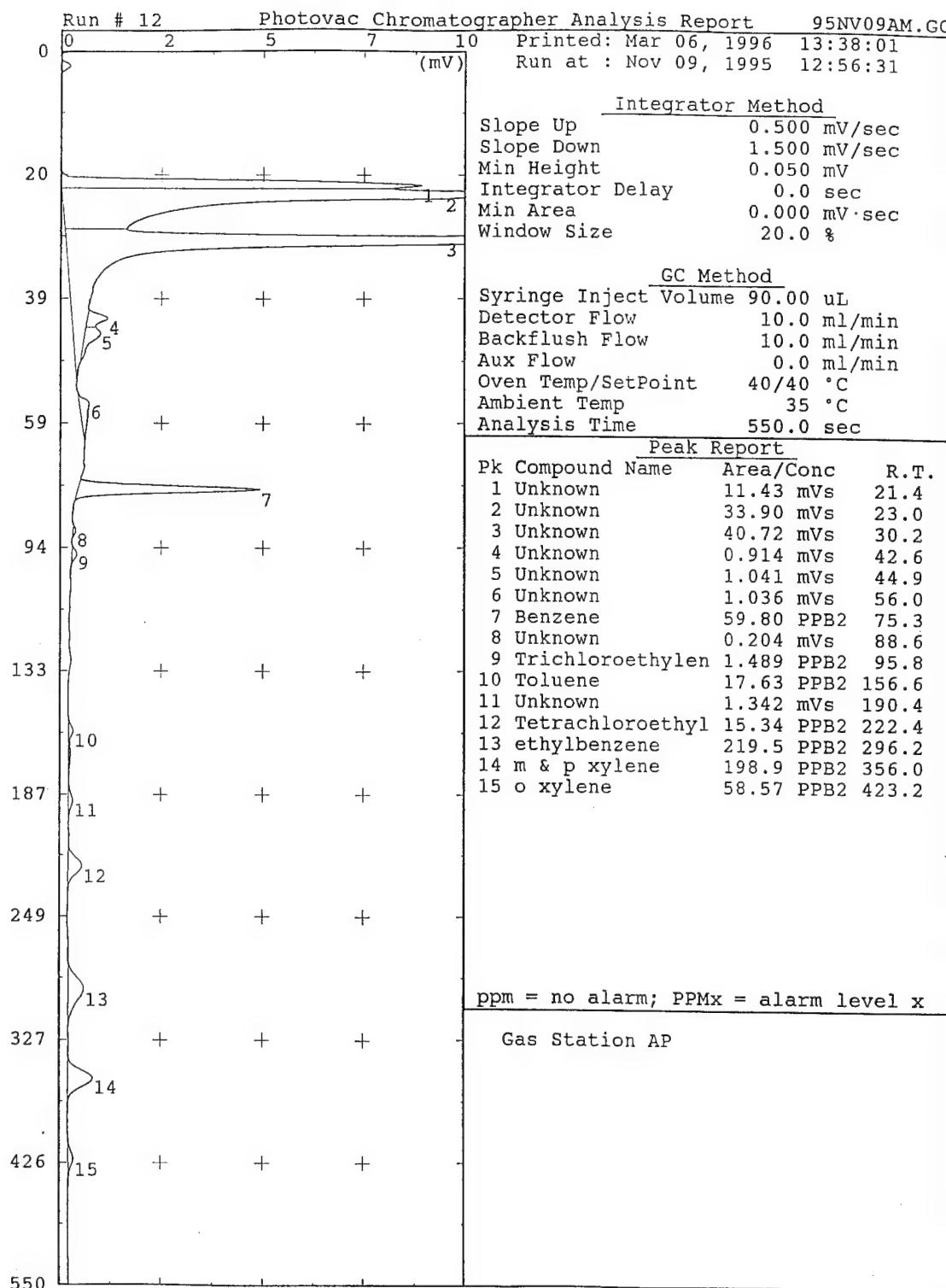


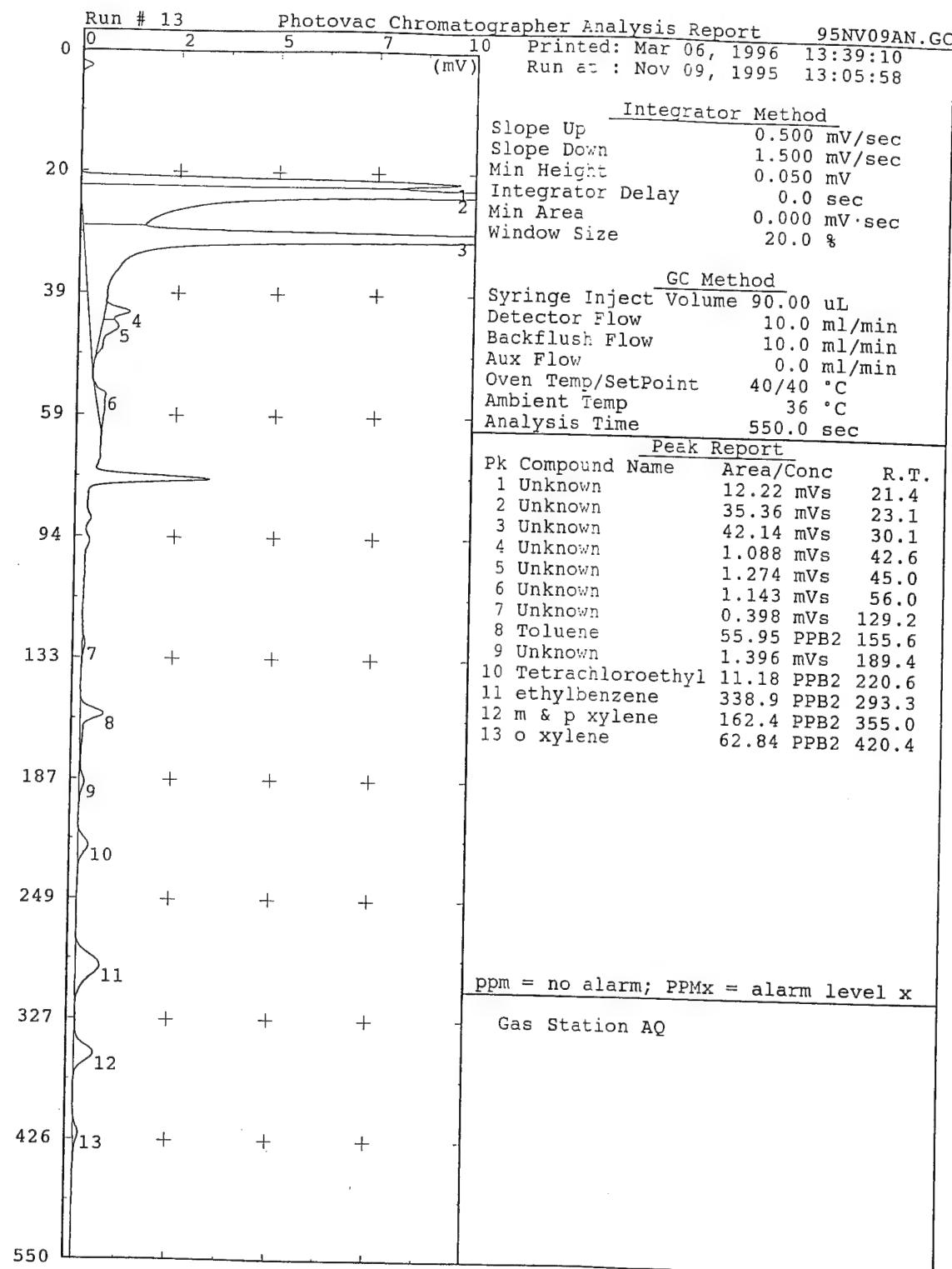


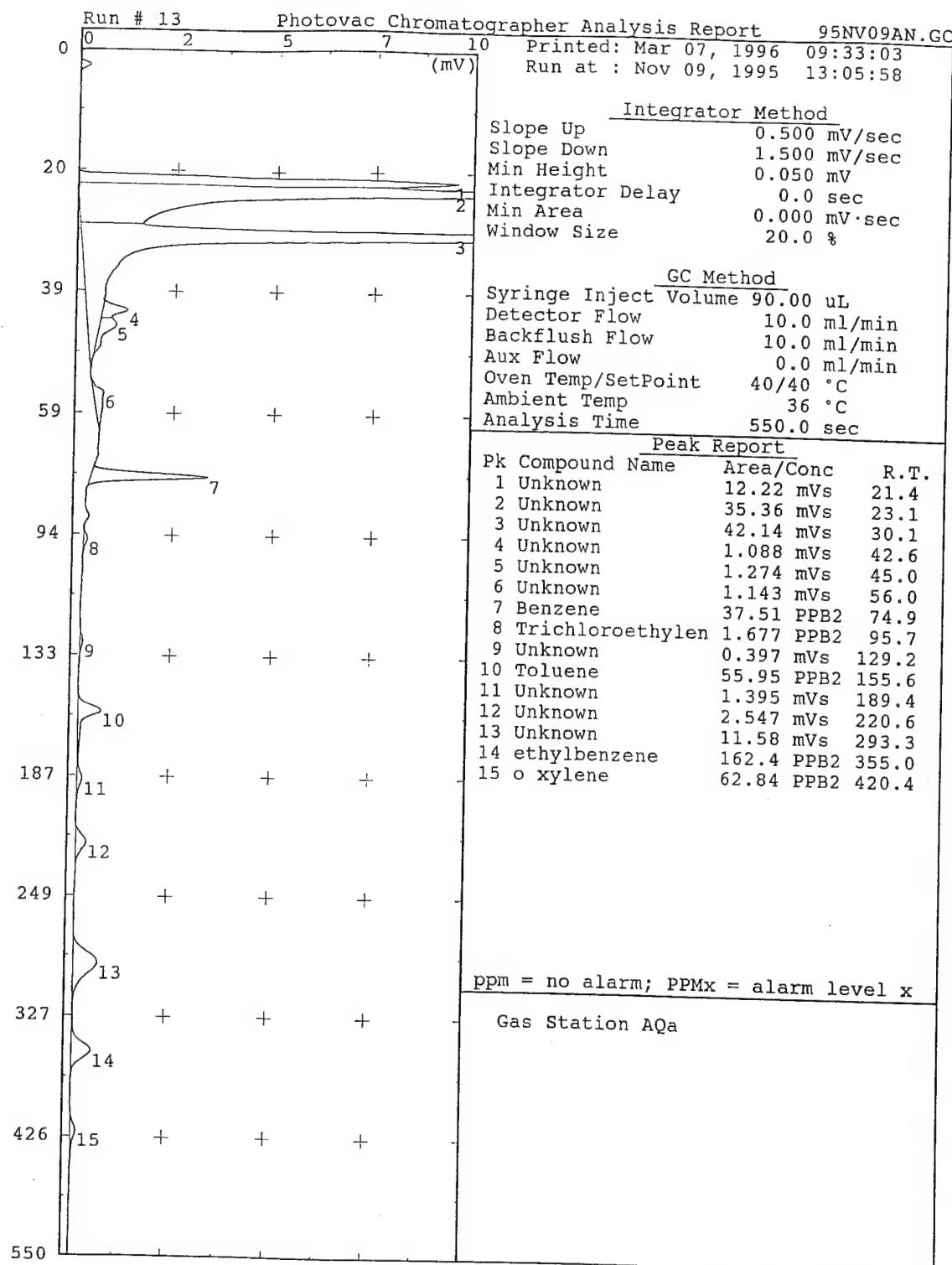


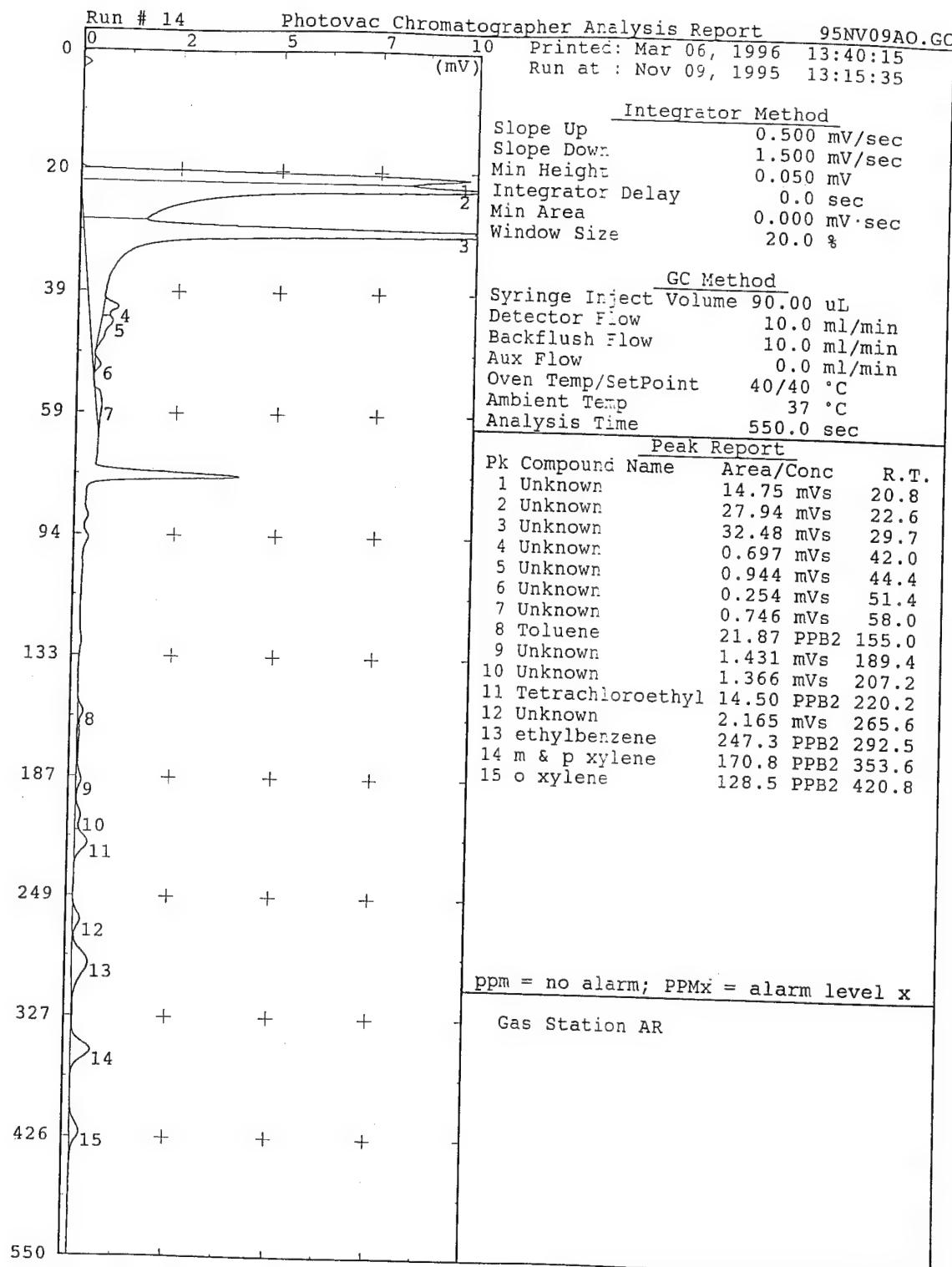


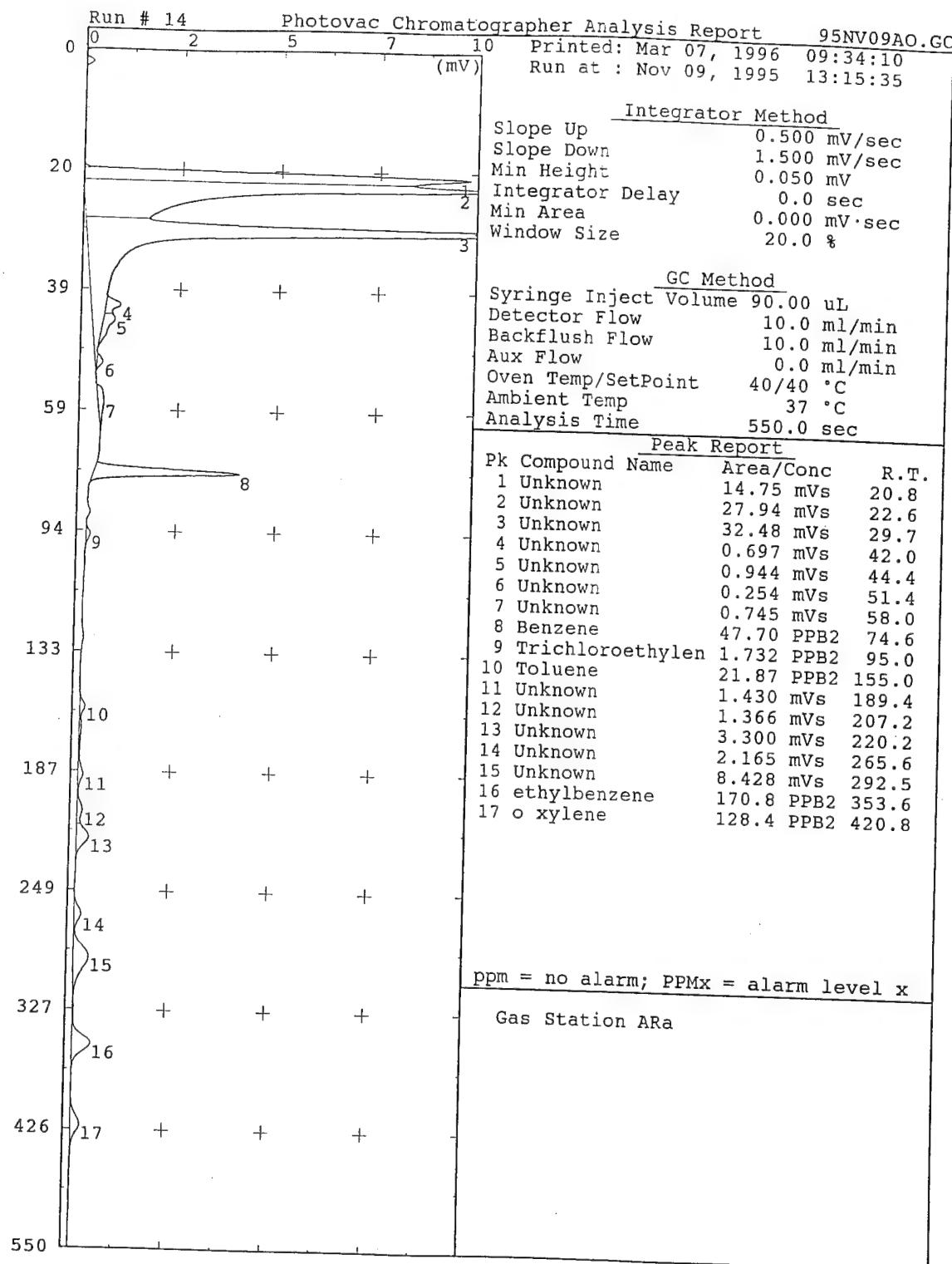


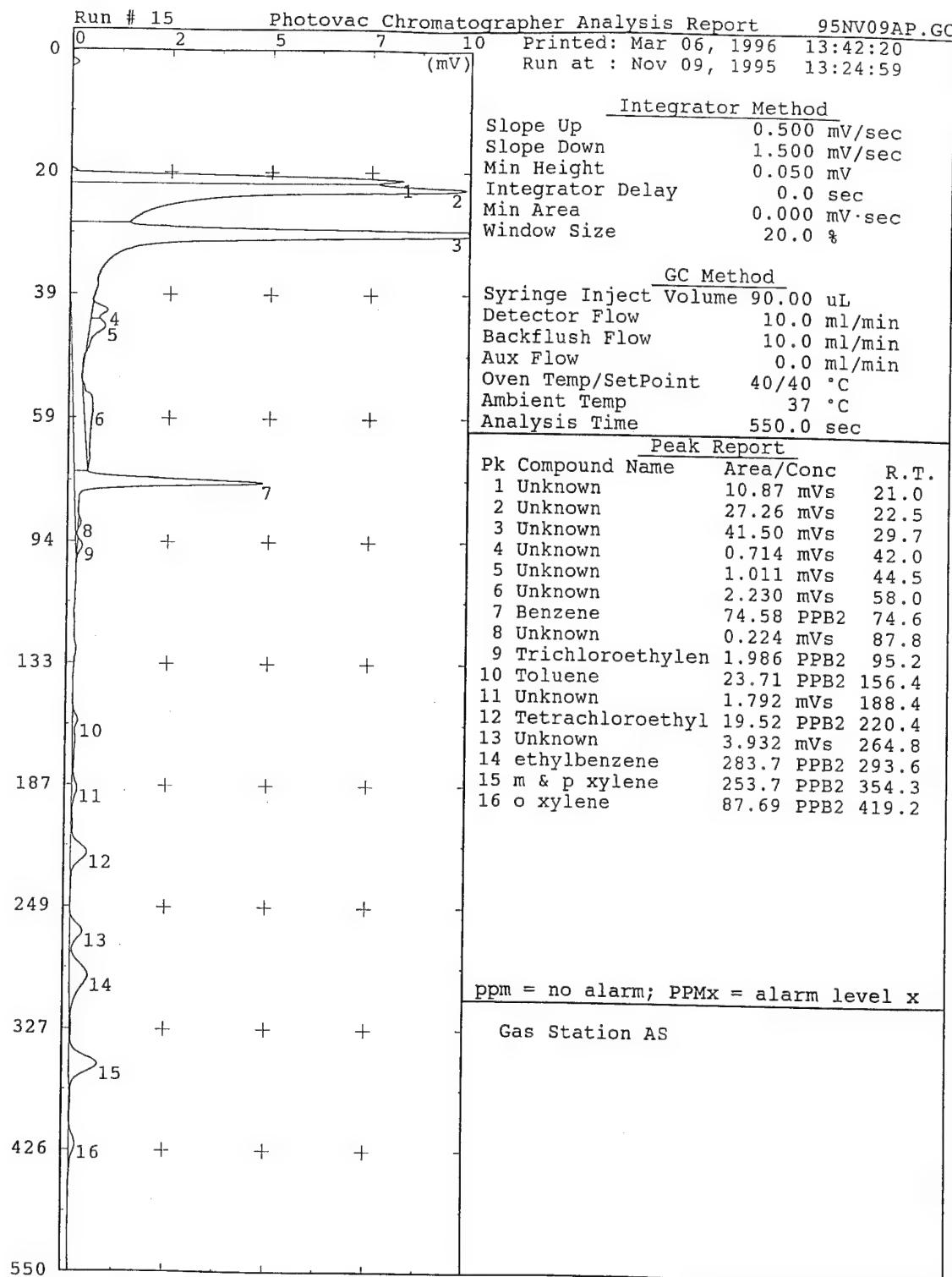


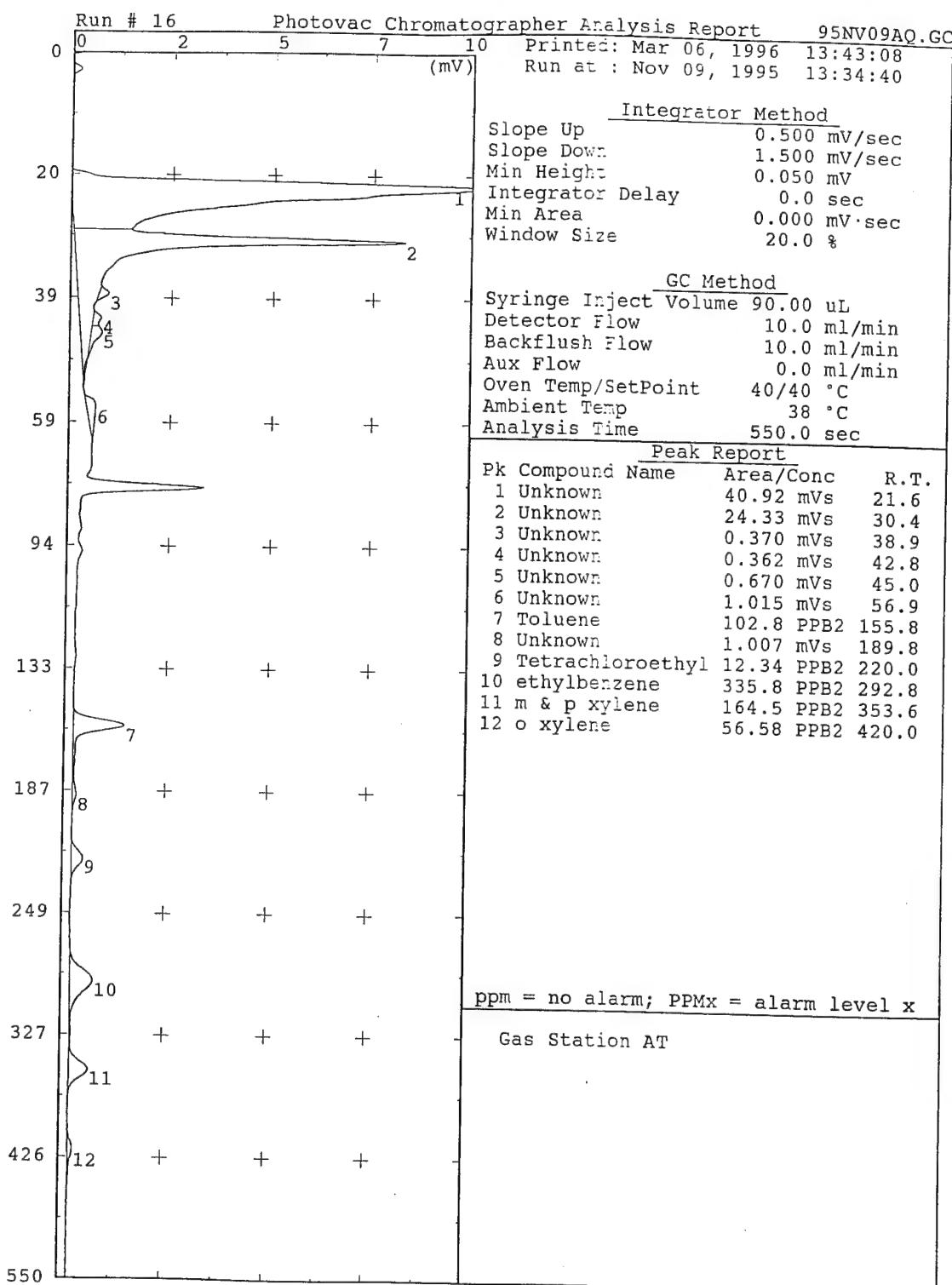


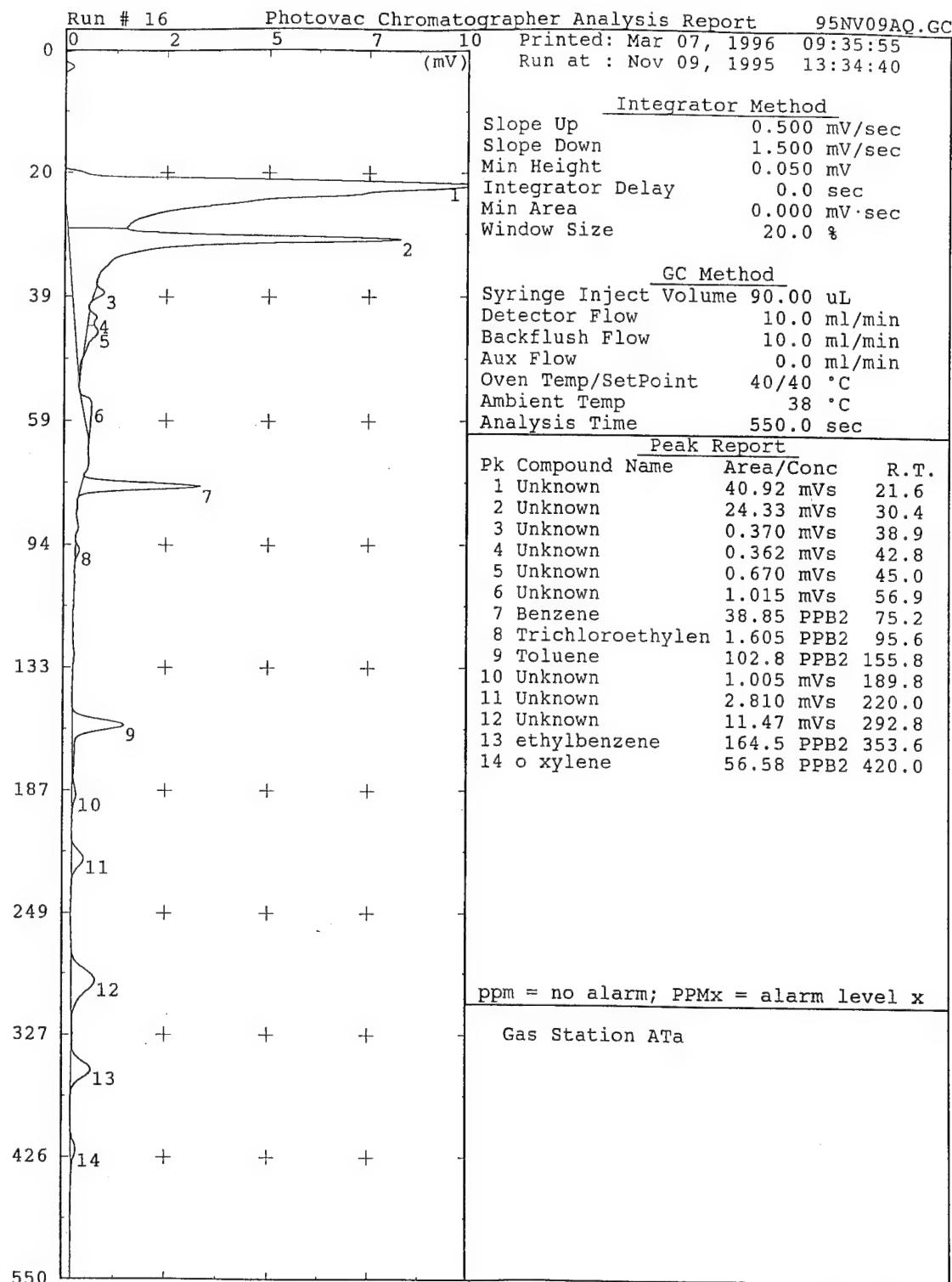


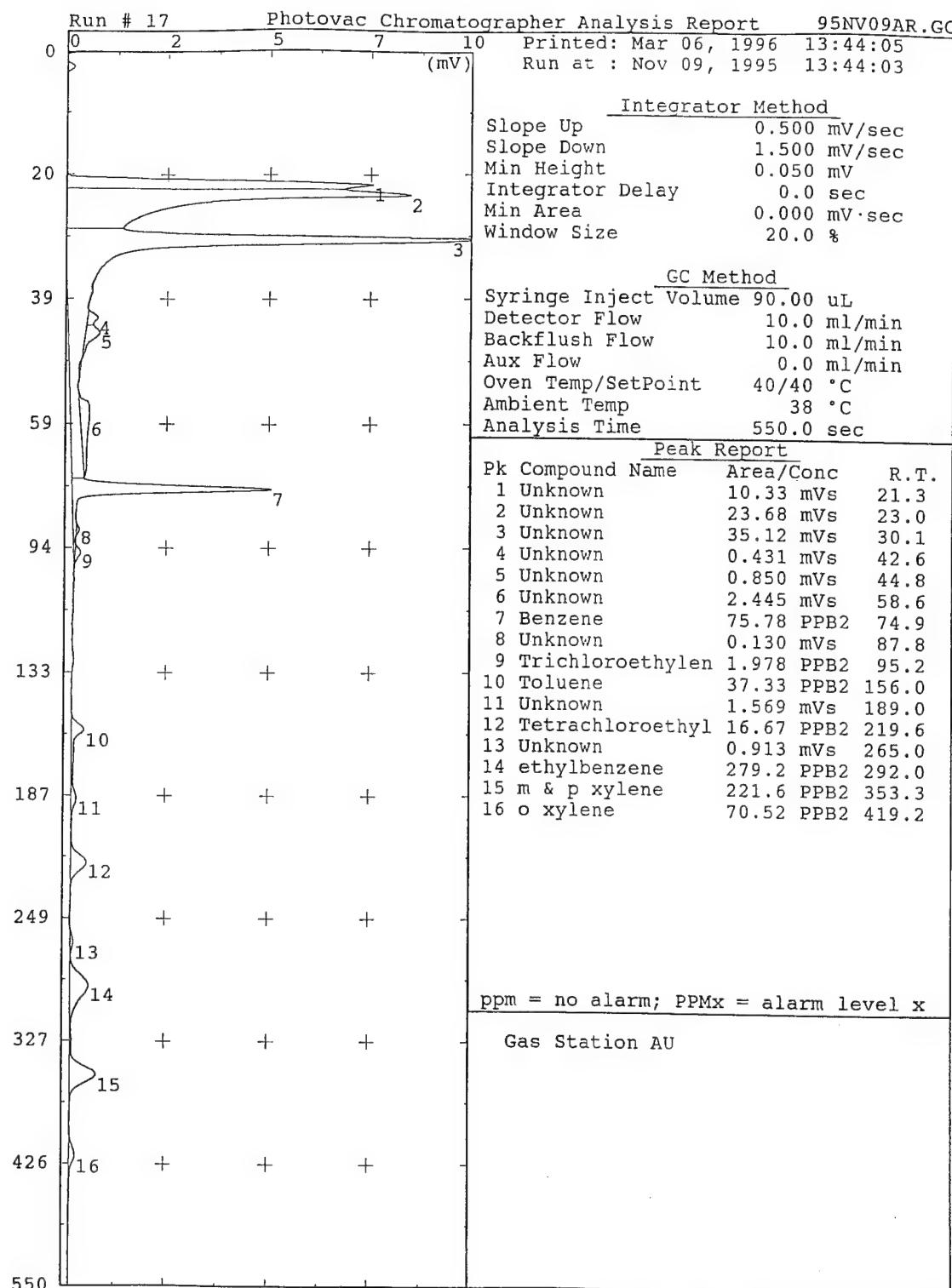


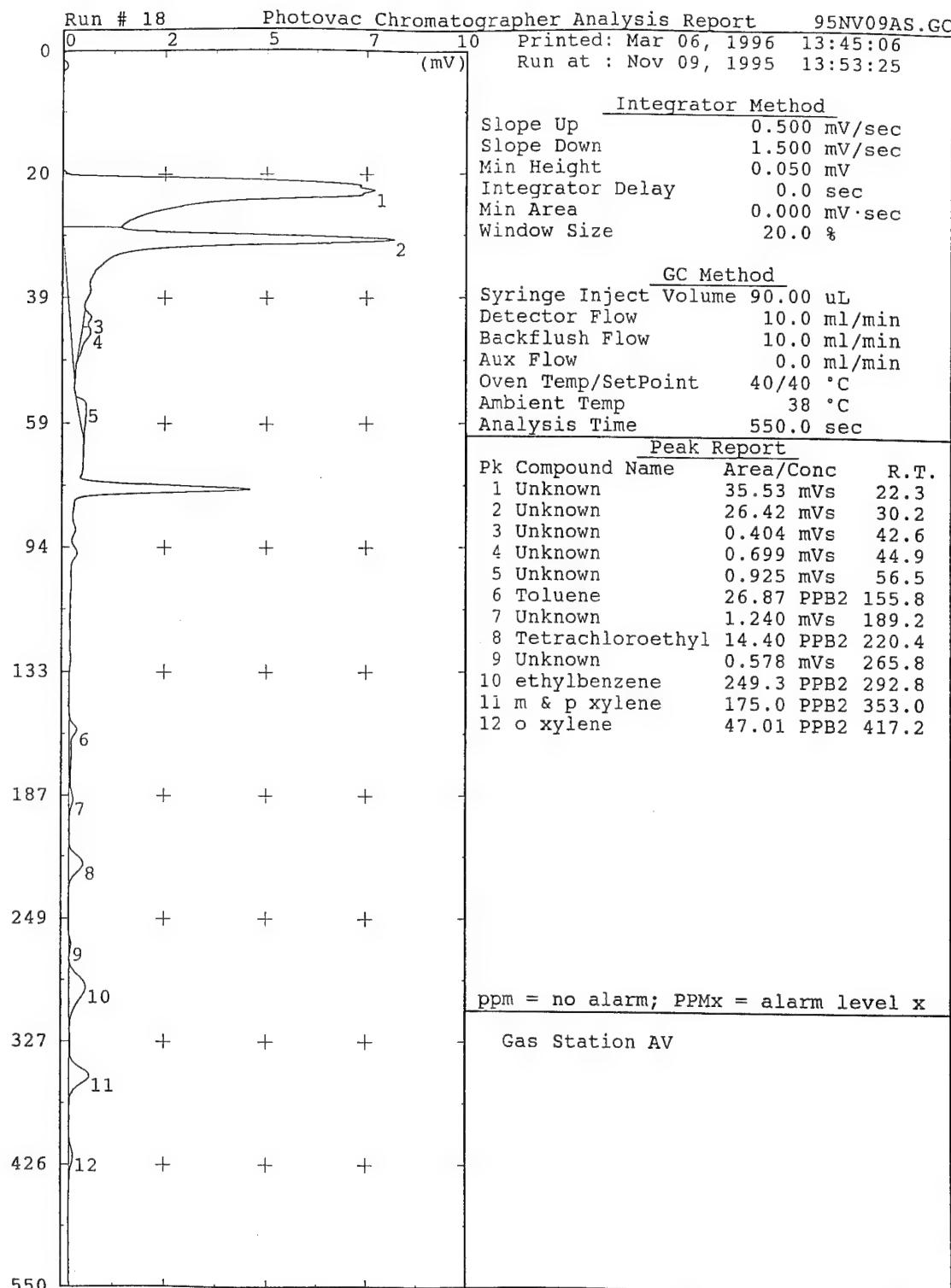


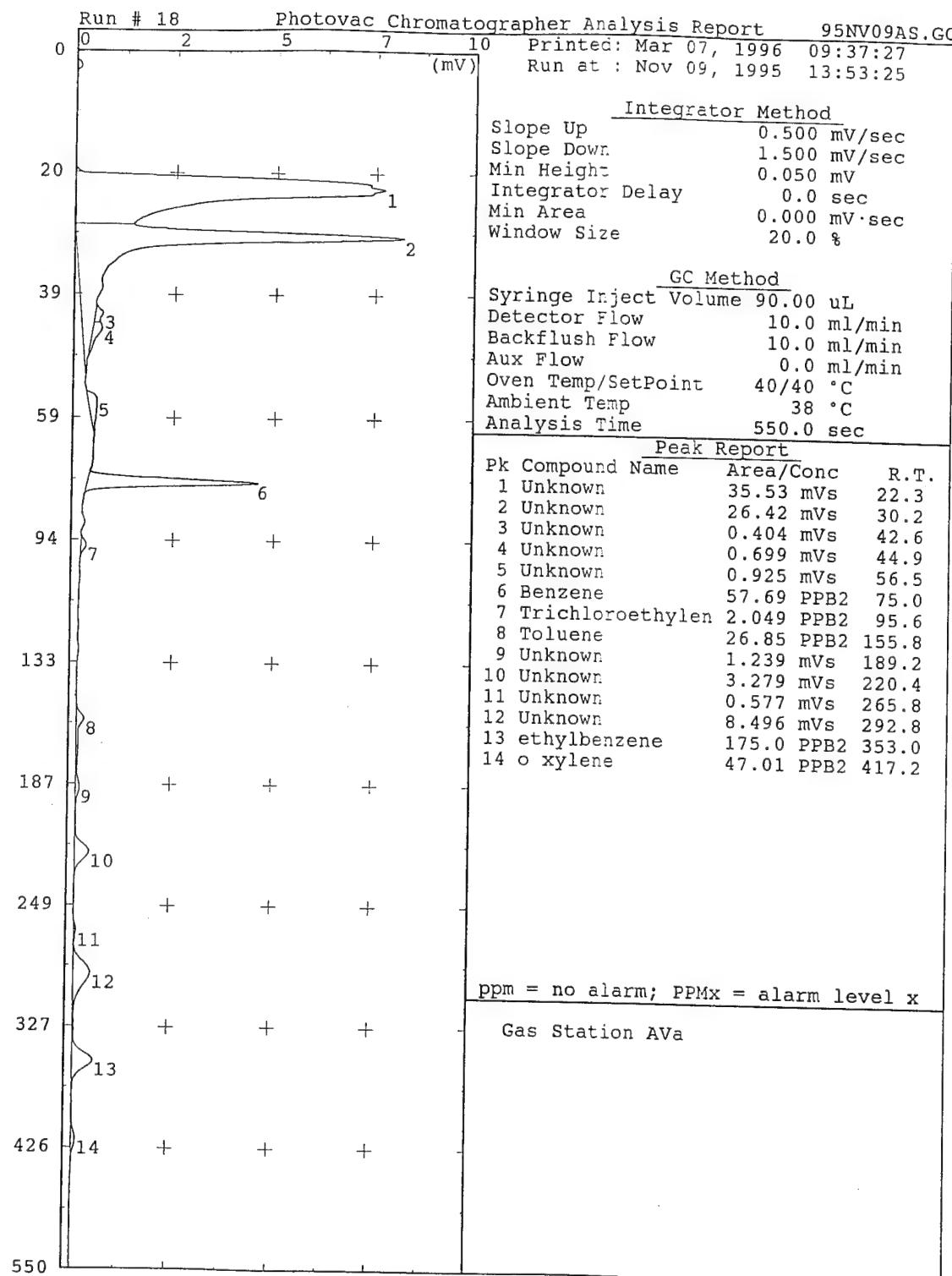


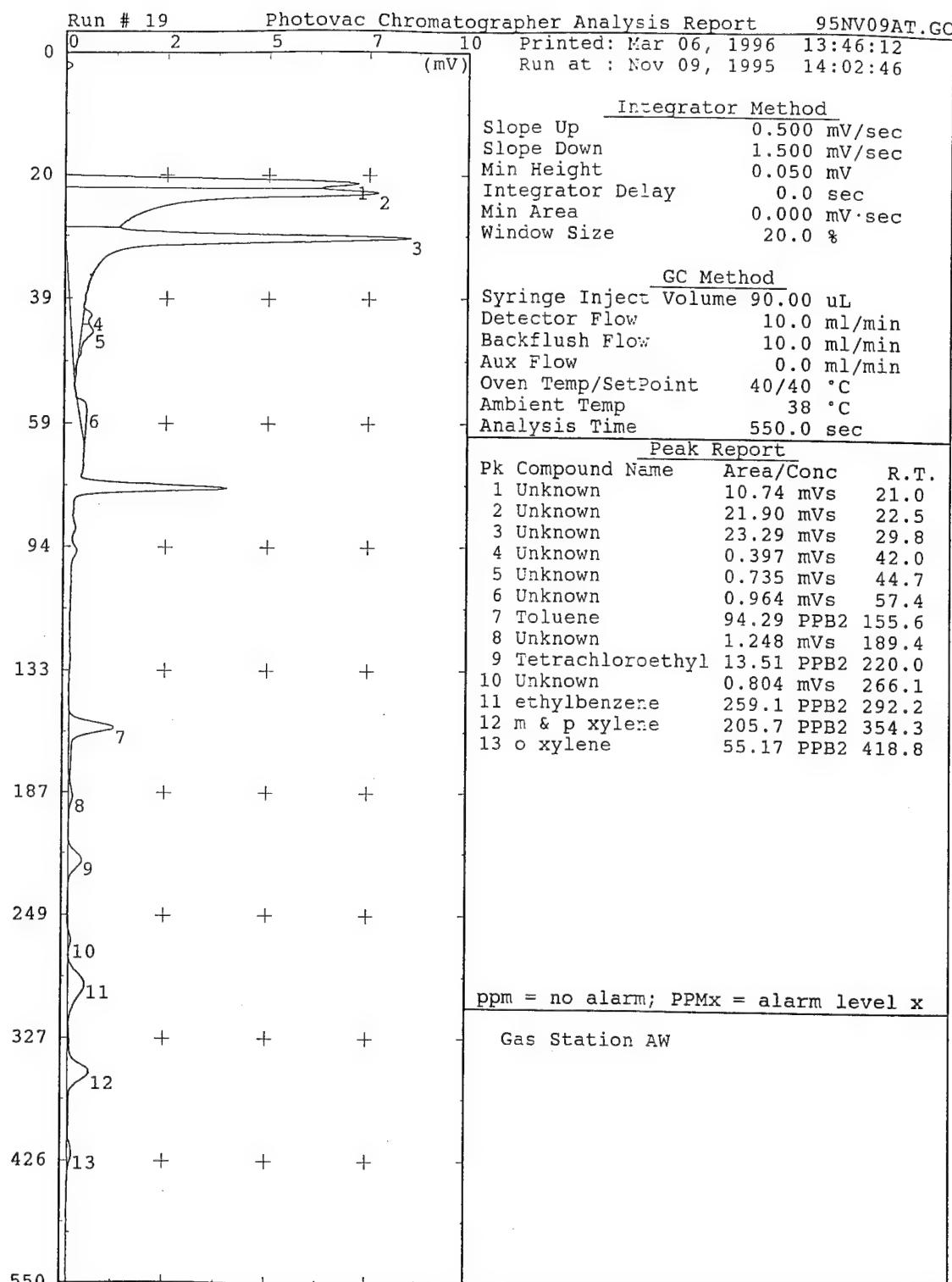


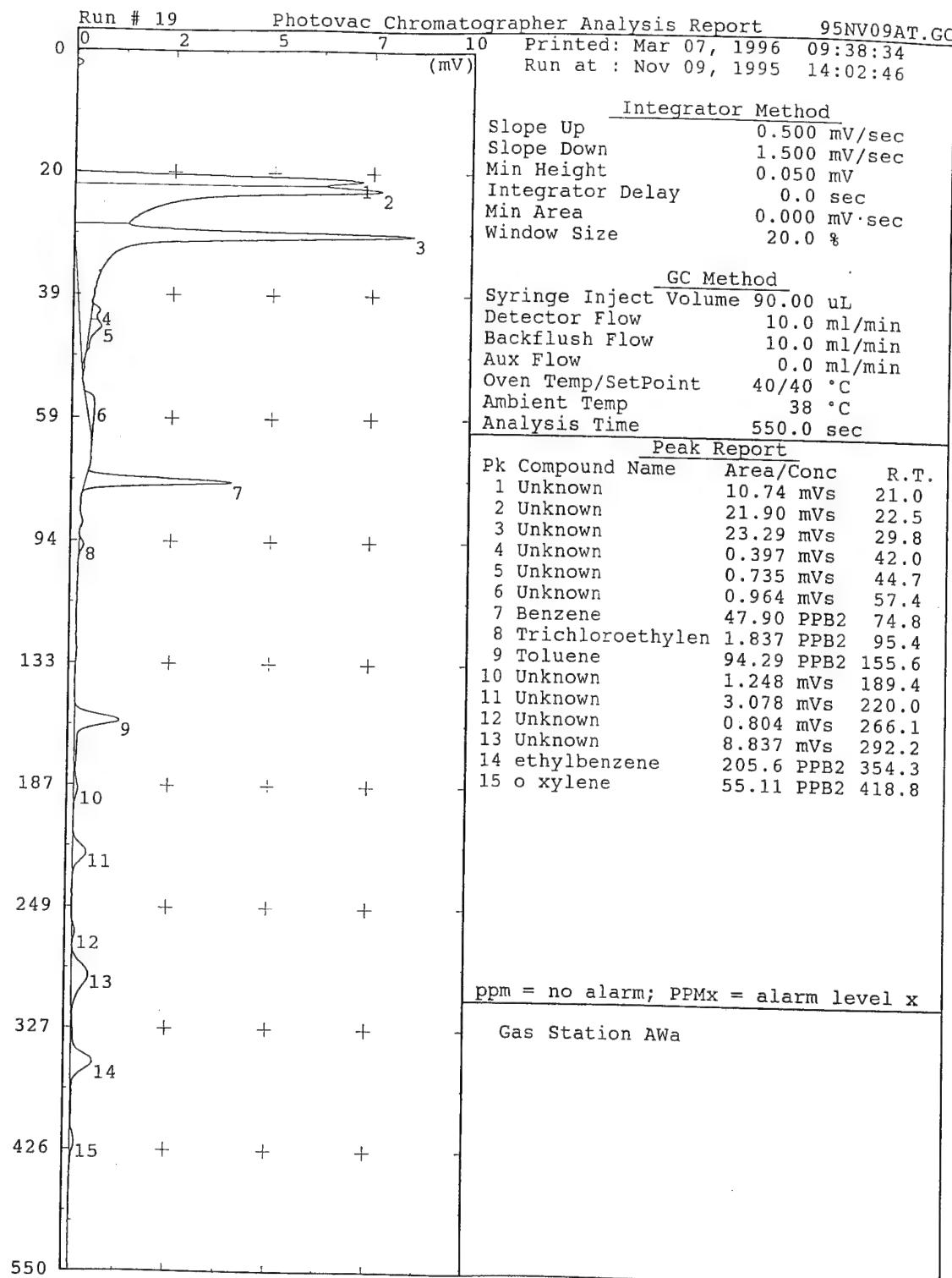






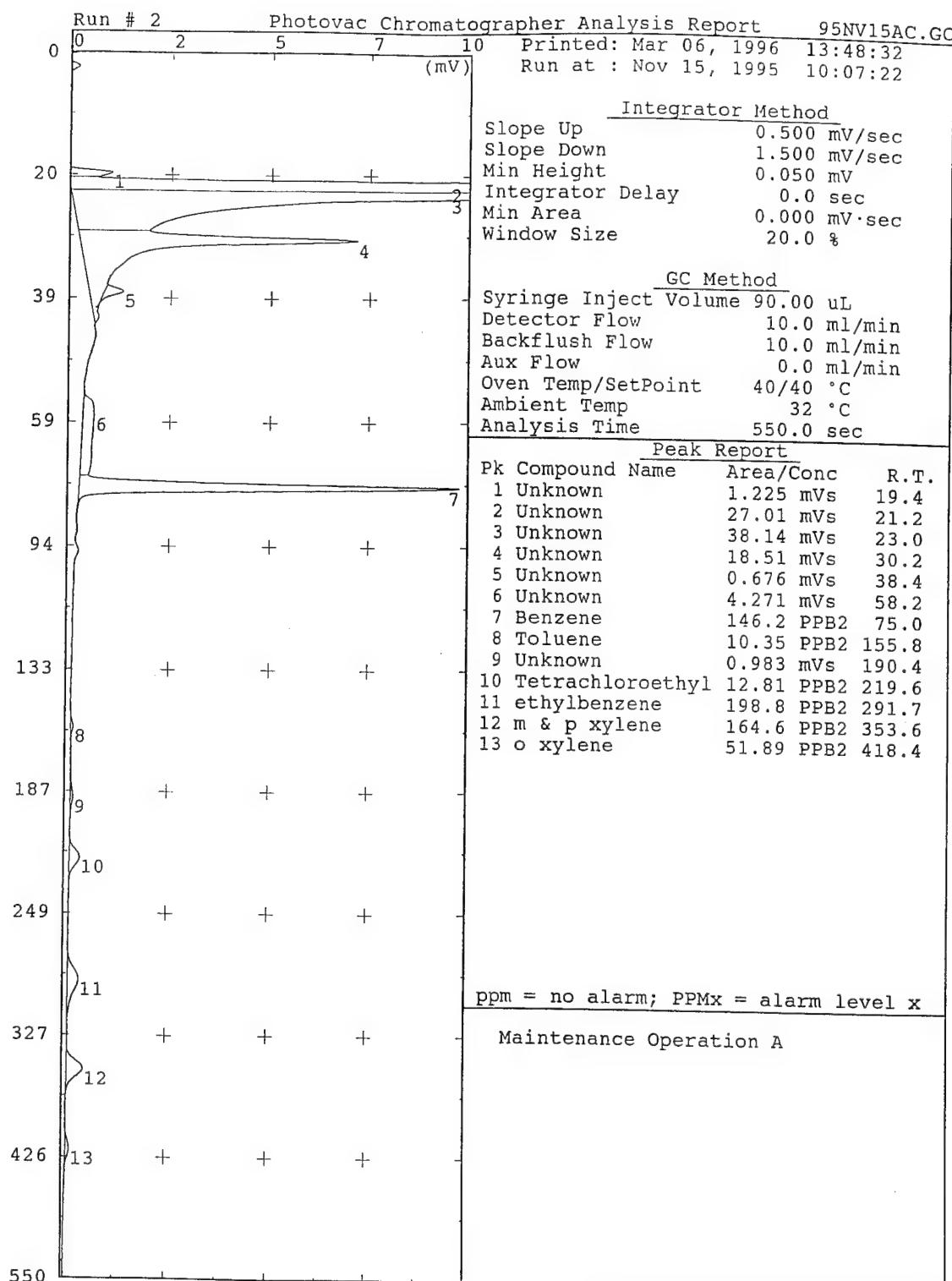


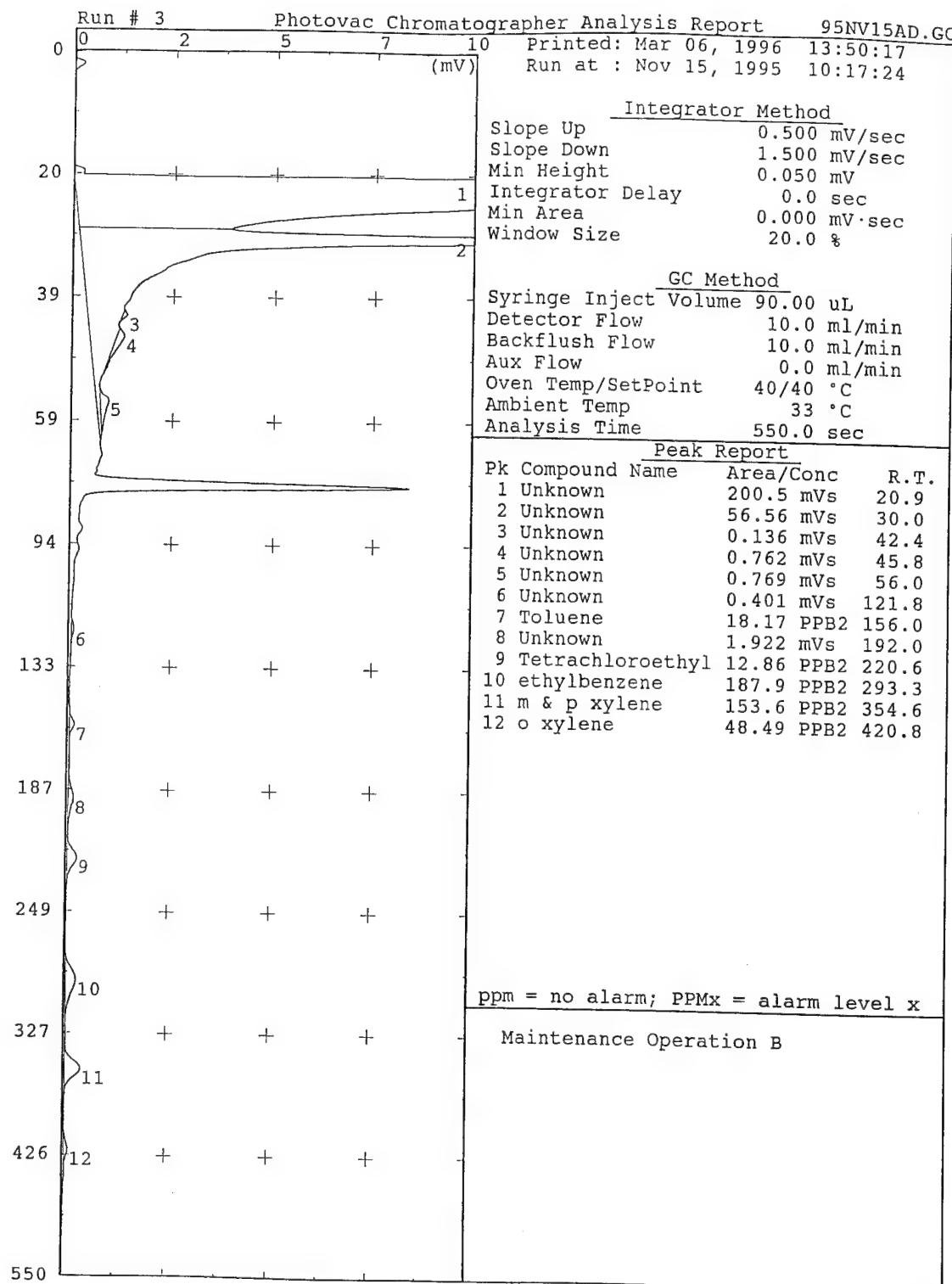


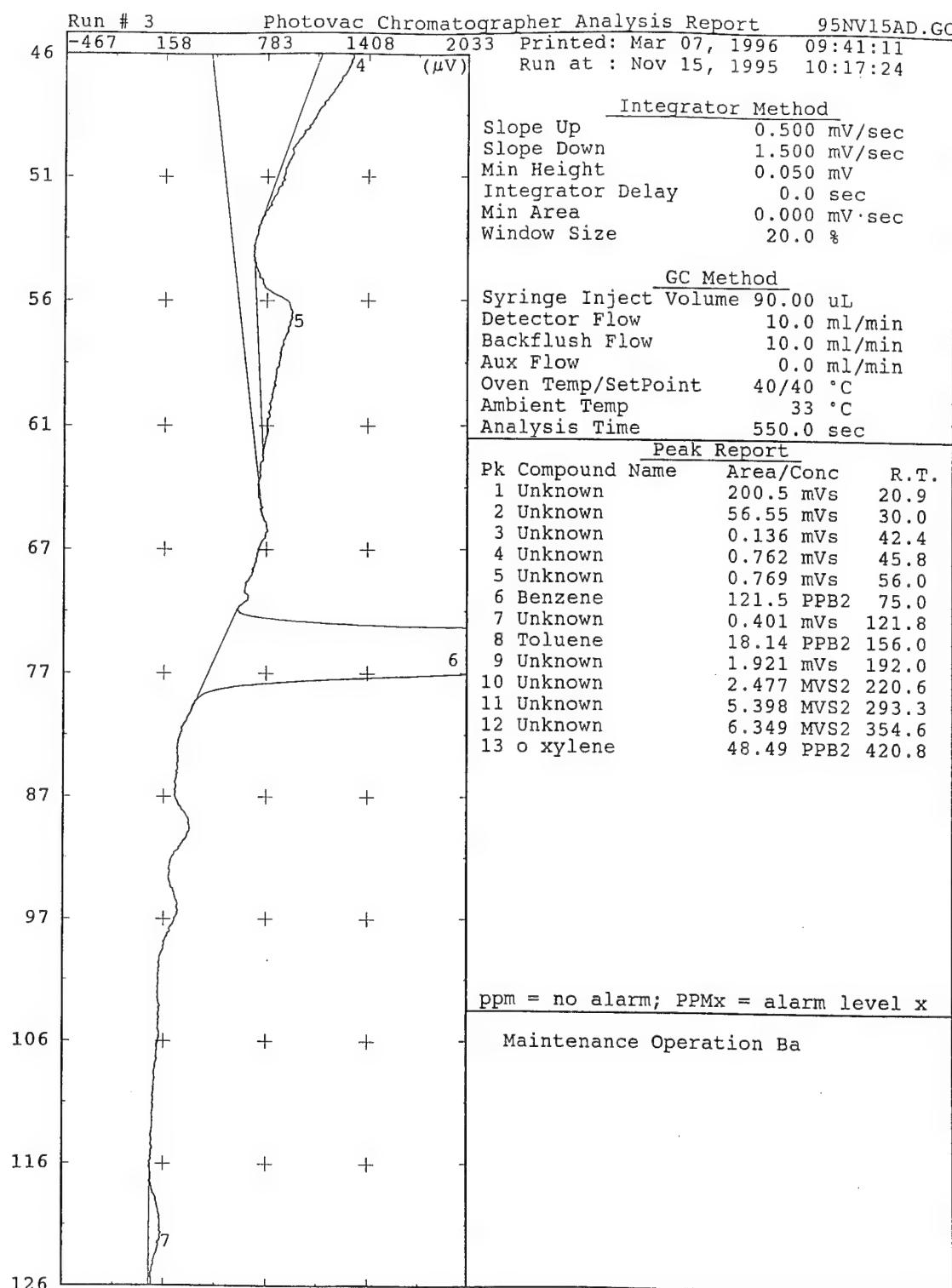


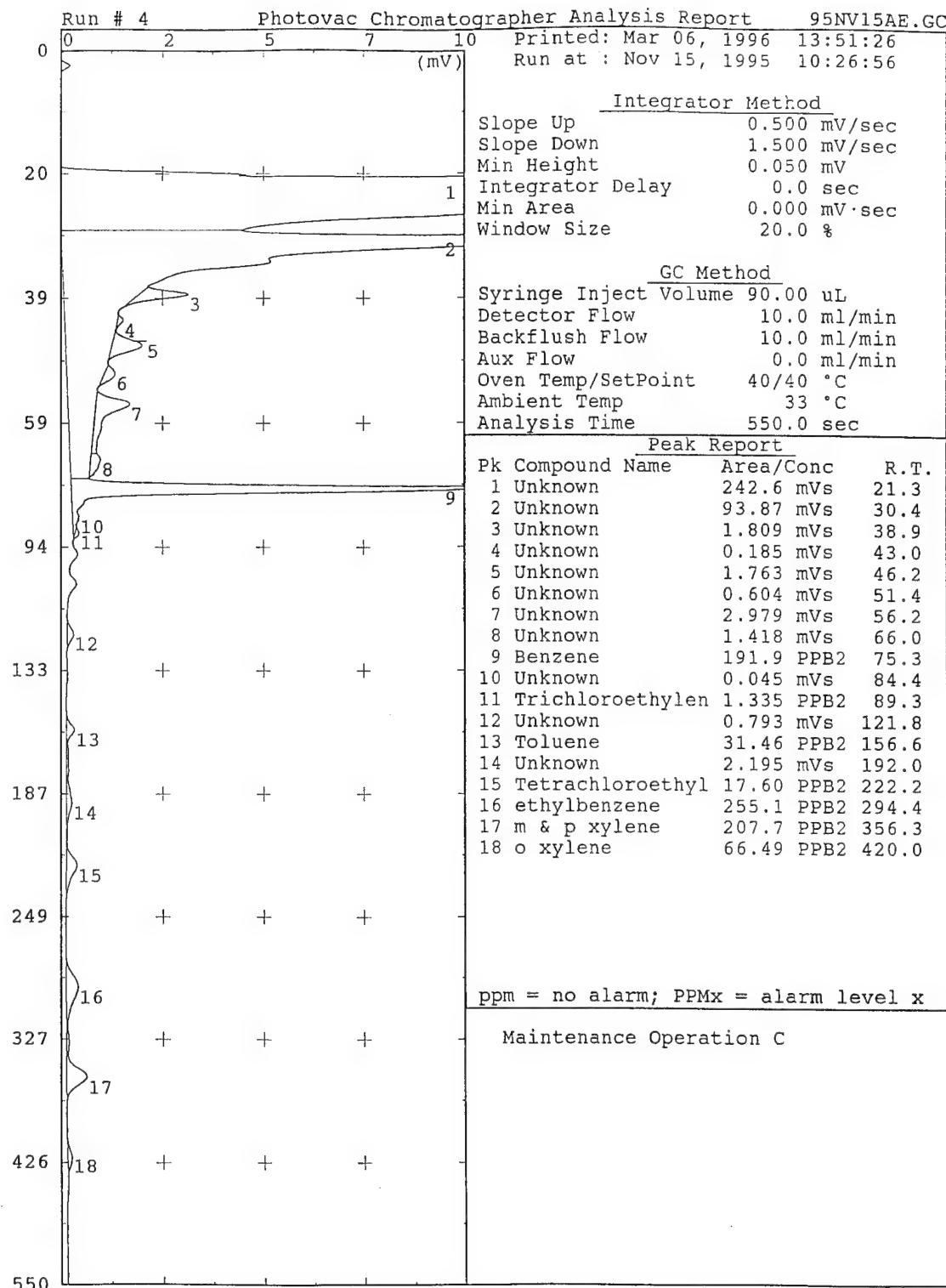
**APPENDIX D**

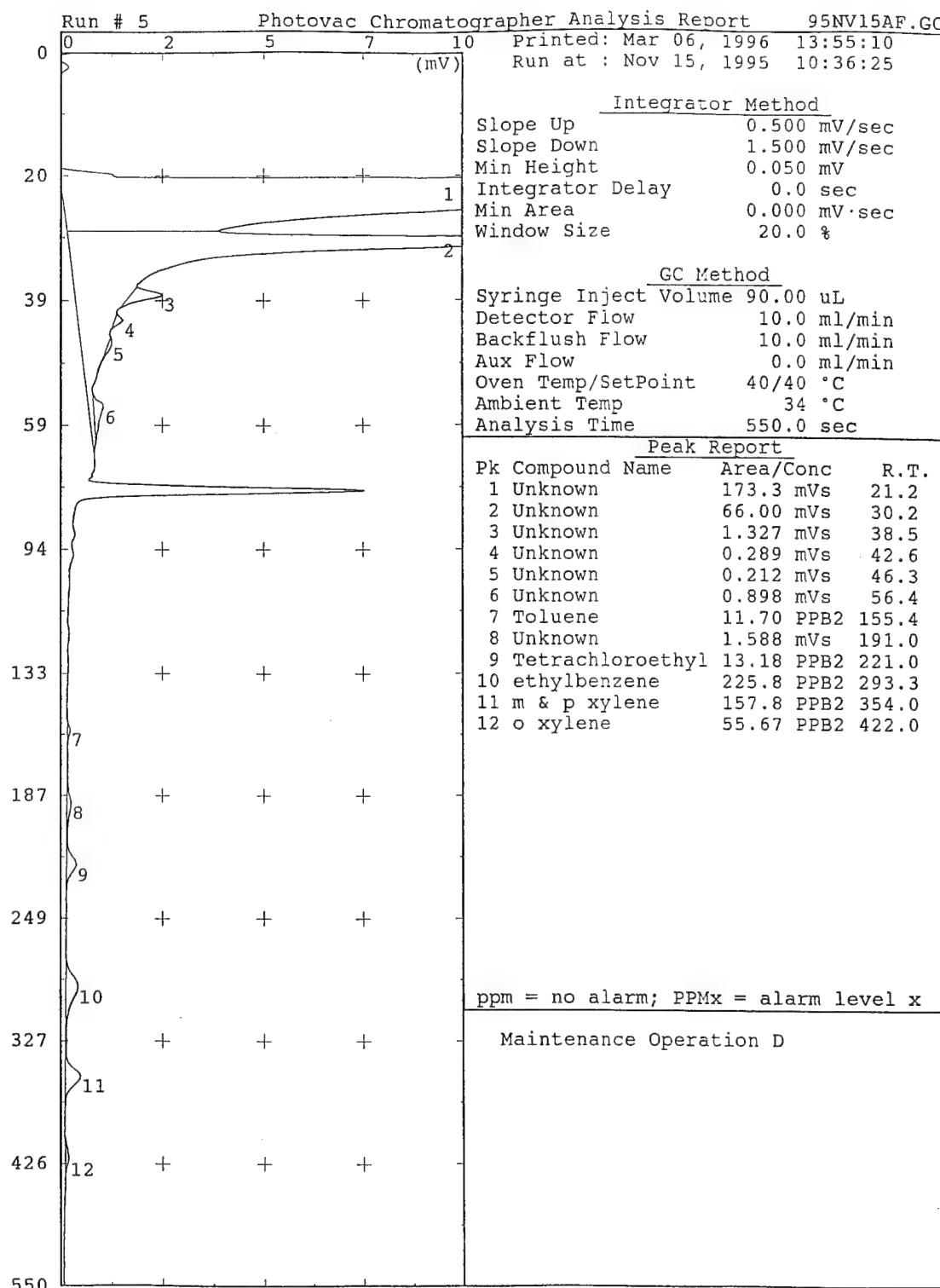
**MAINTENANCE OPERATION CHROMATOGRAMS**

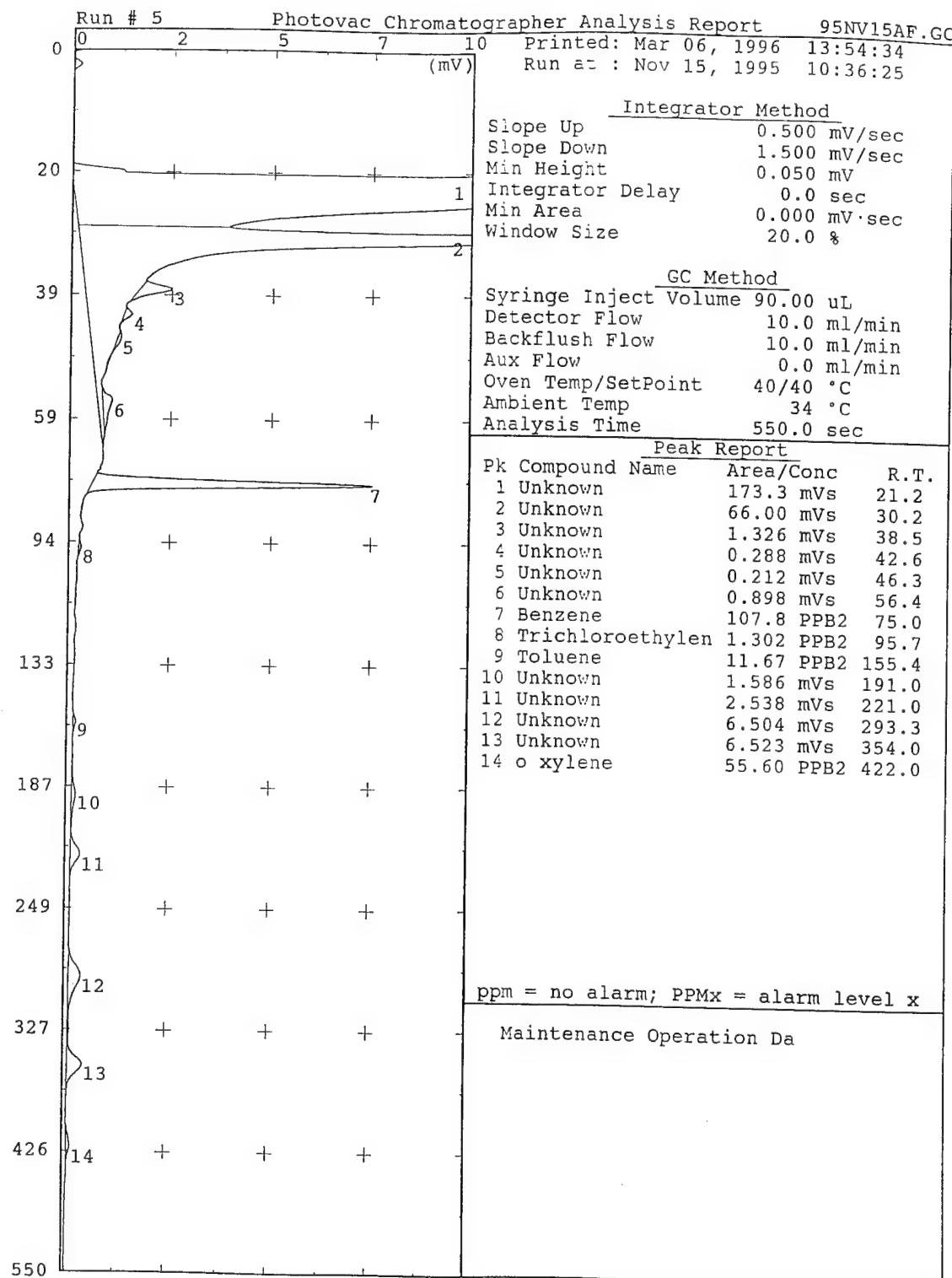


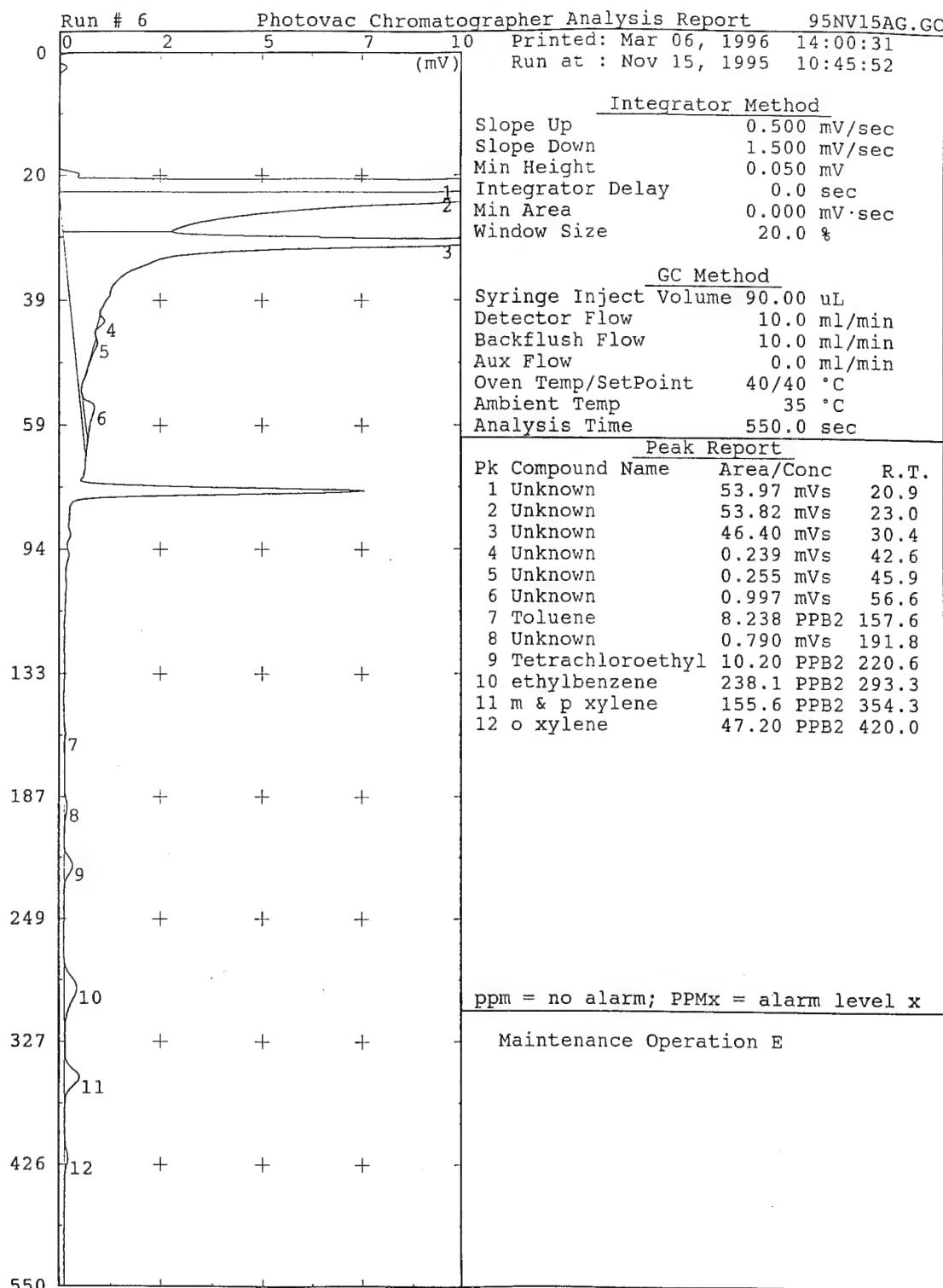


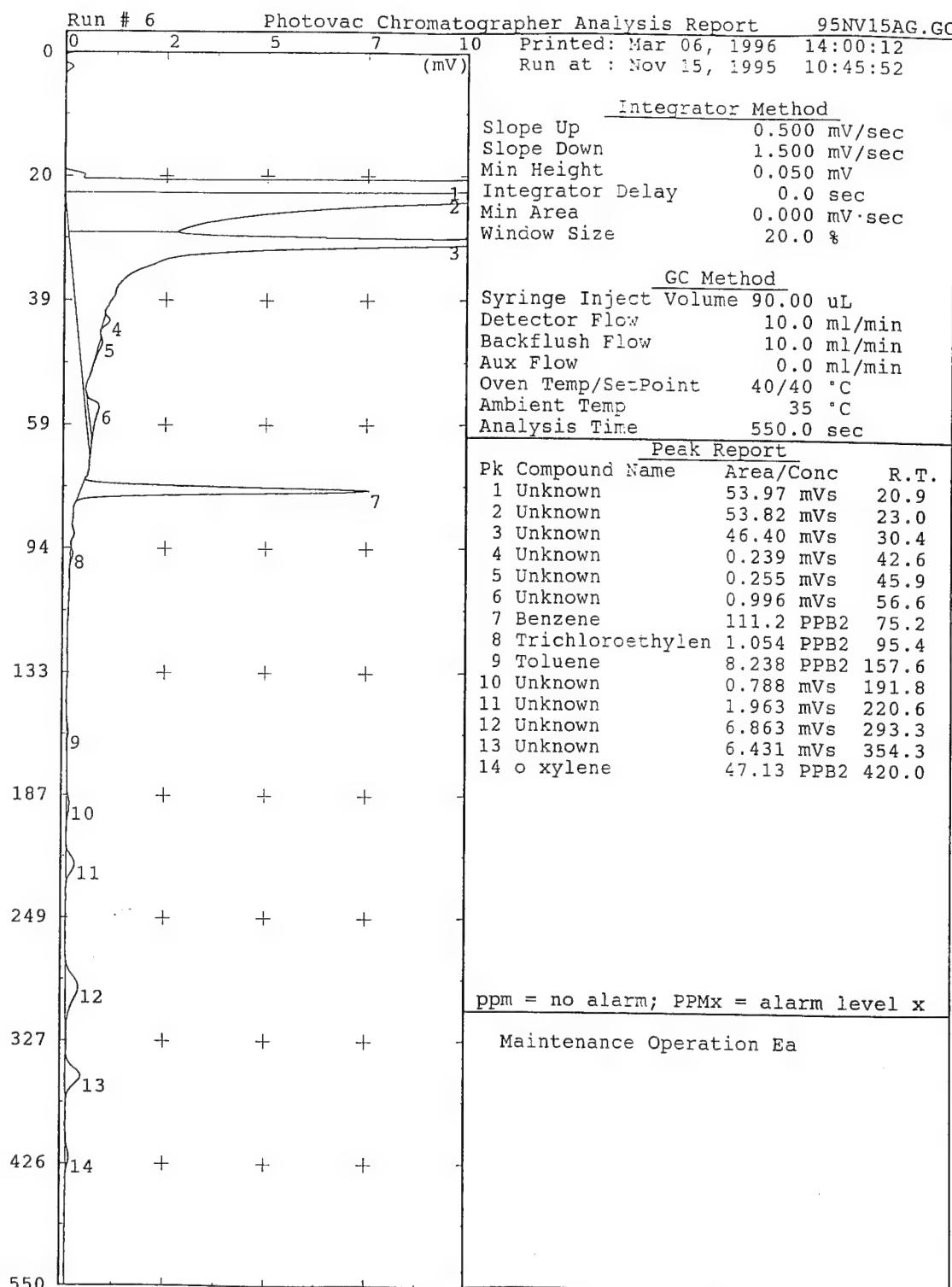


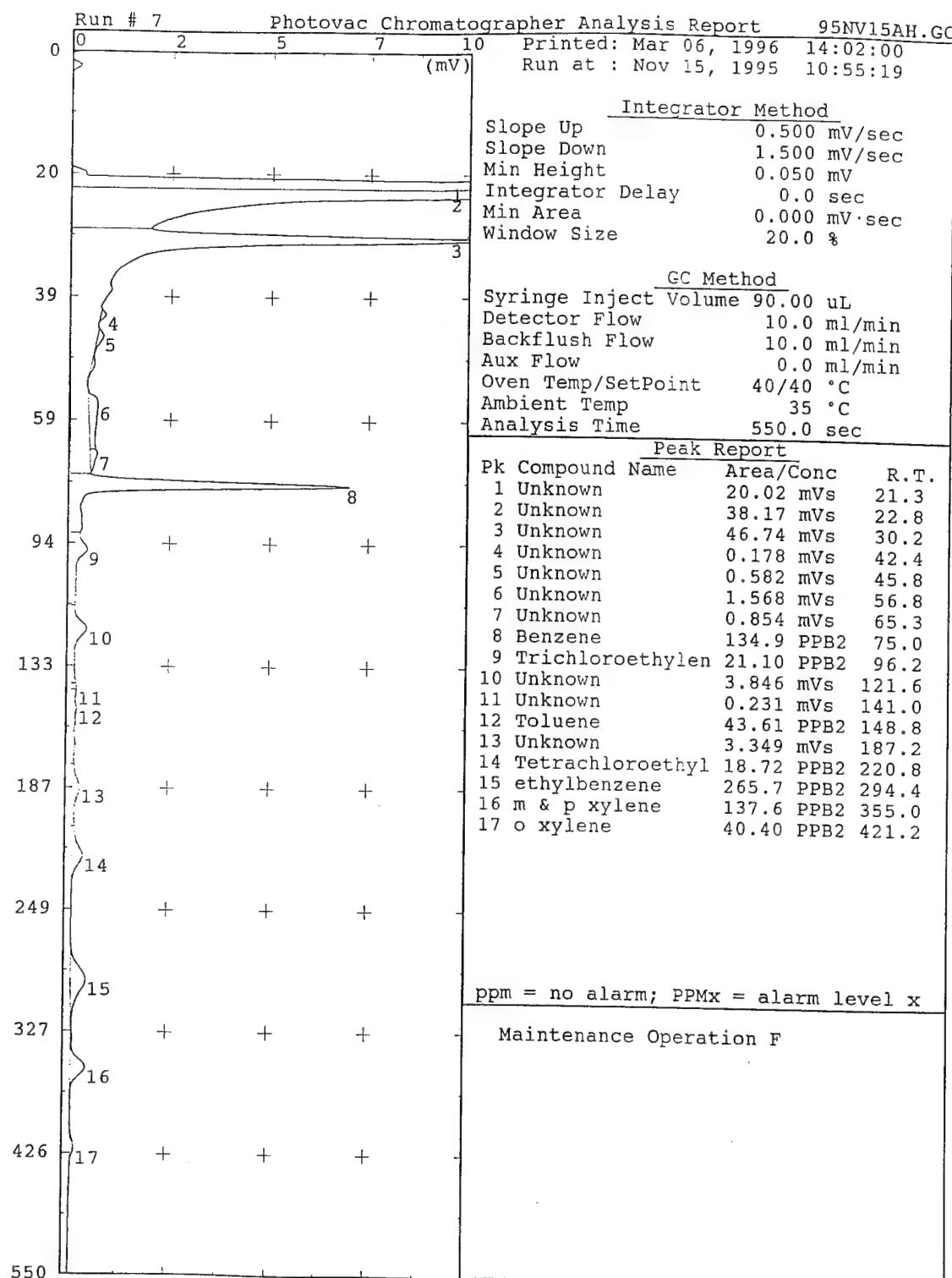


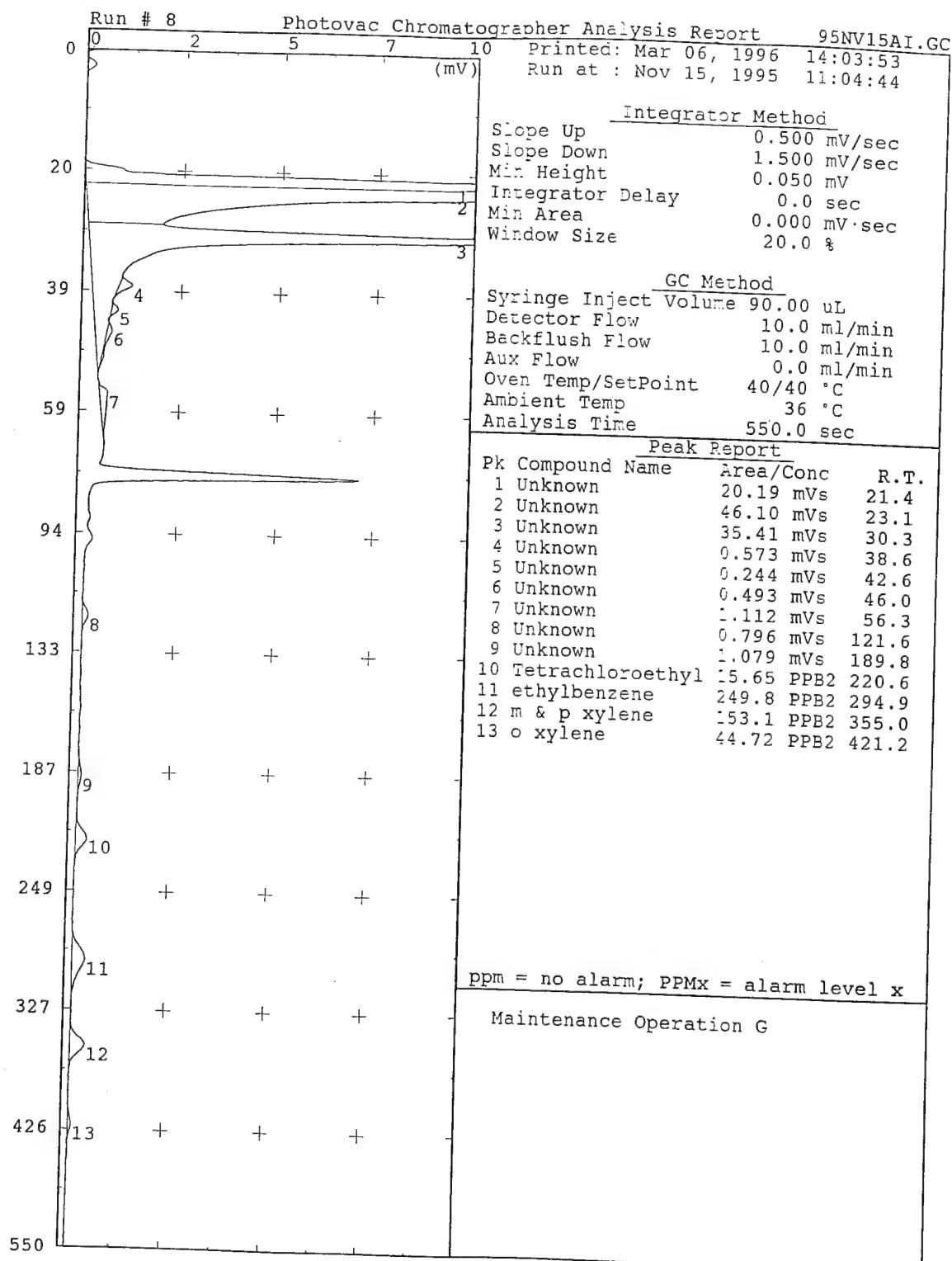


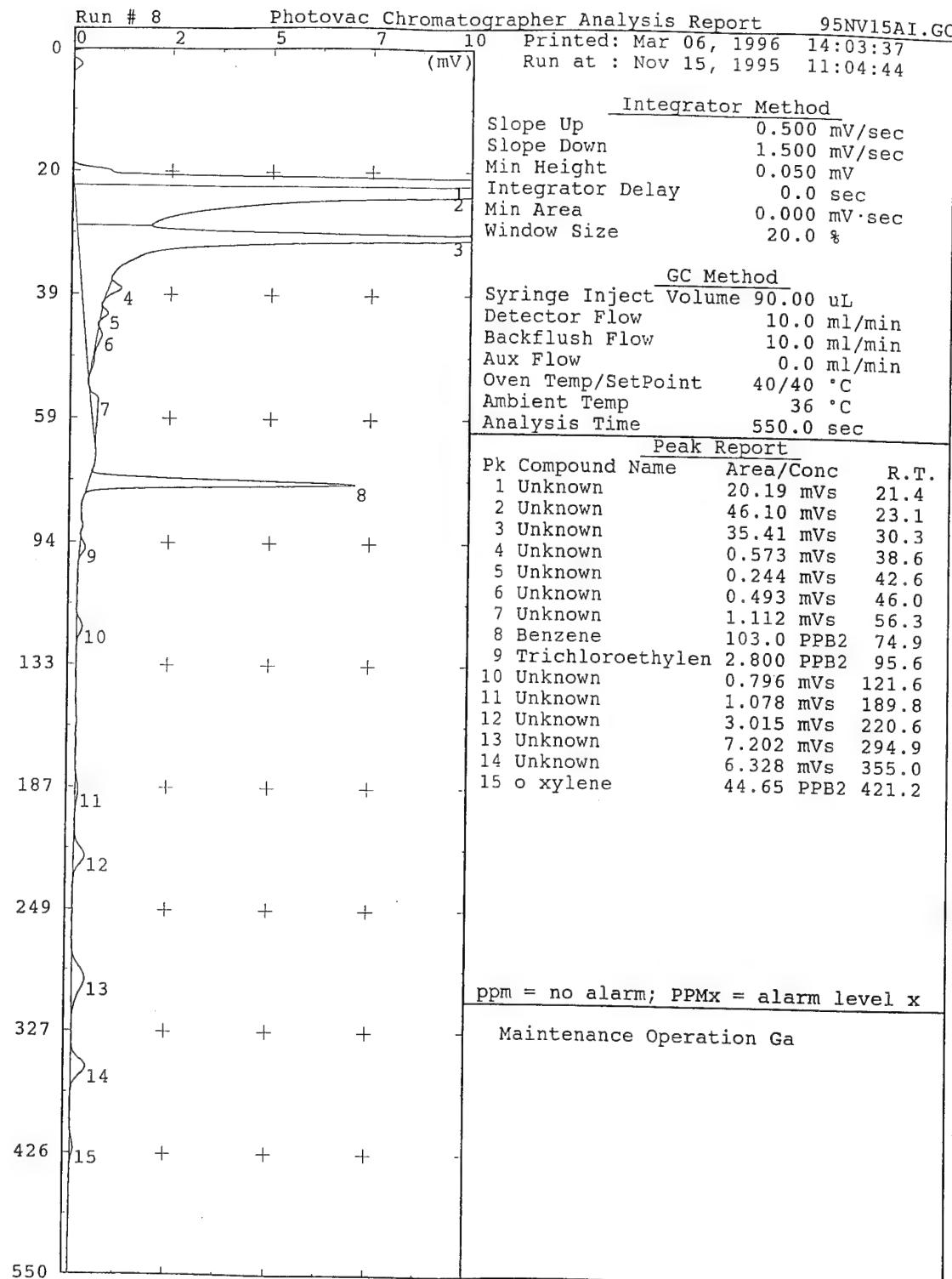


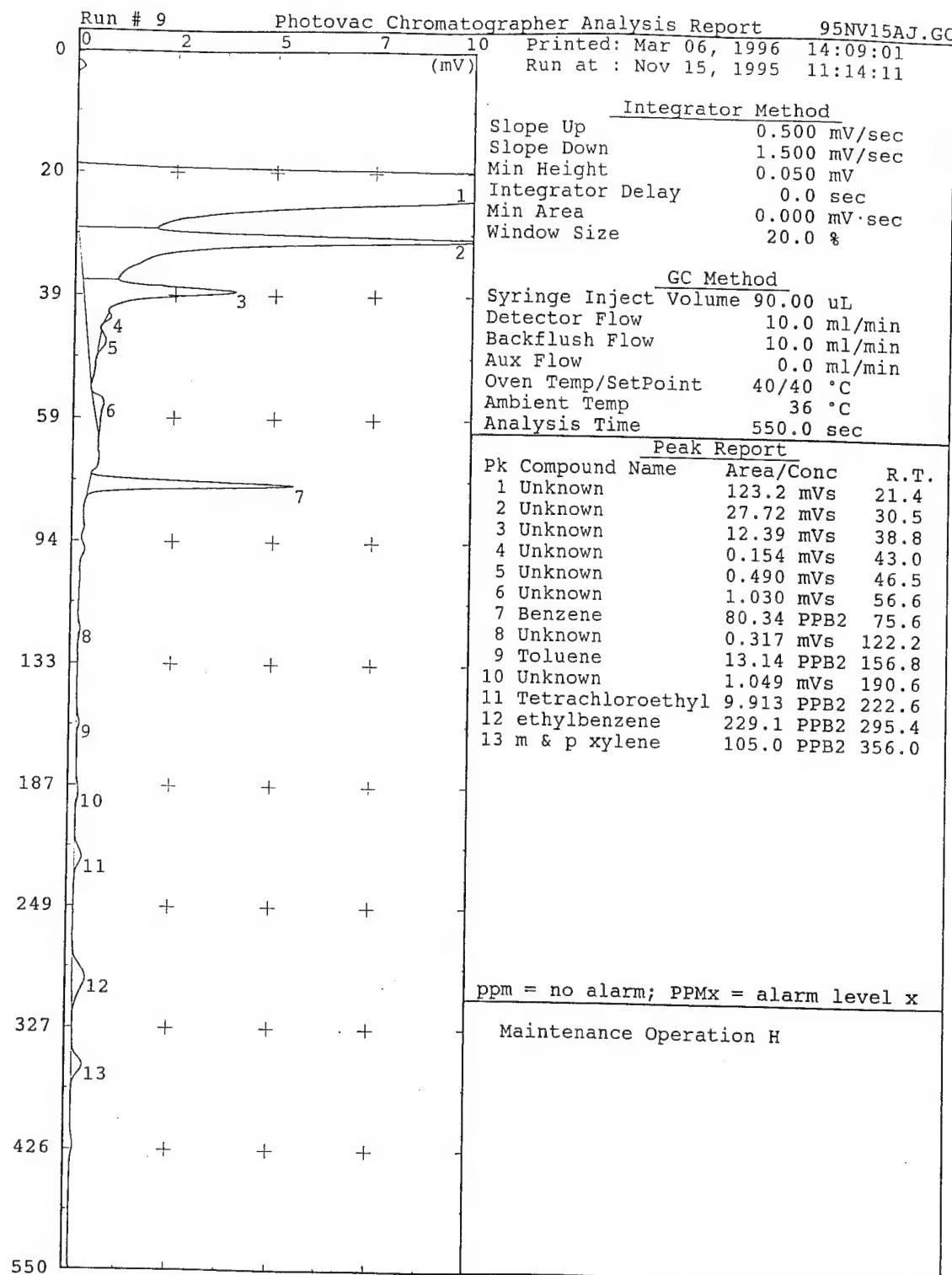


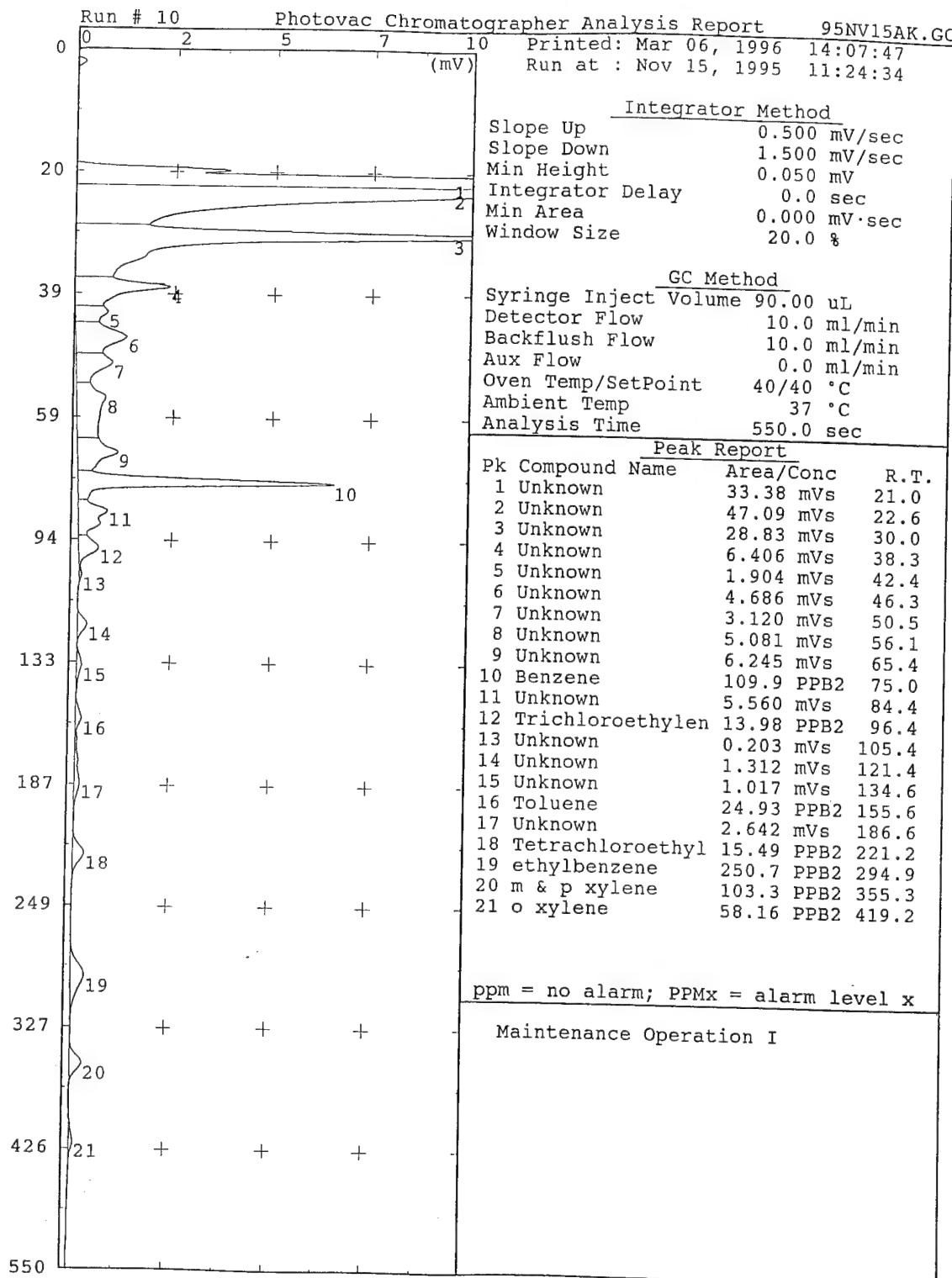


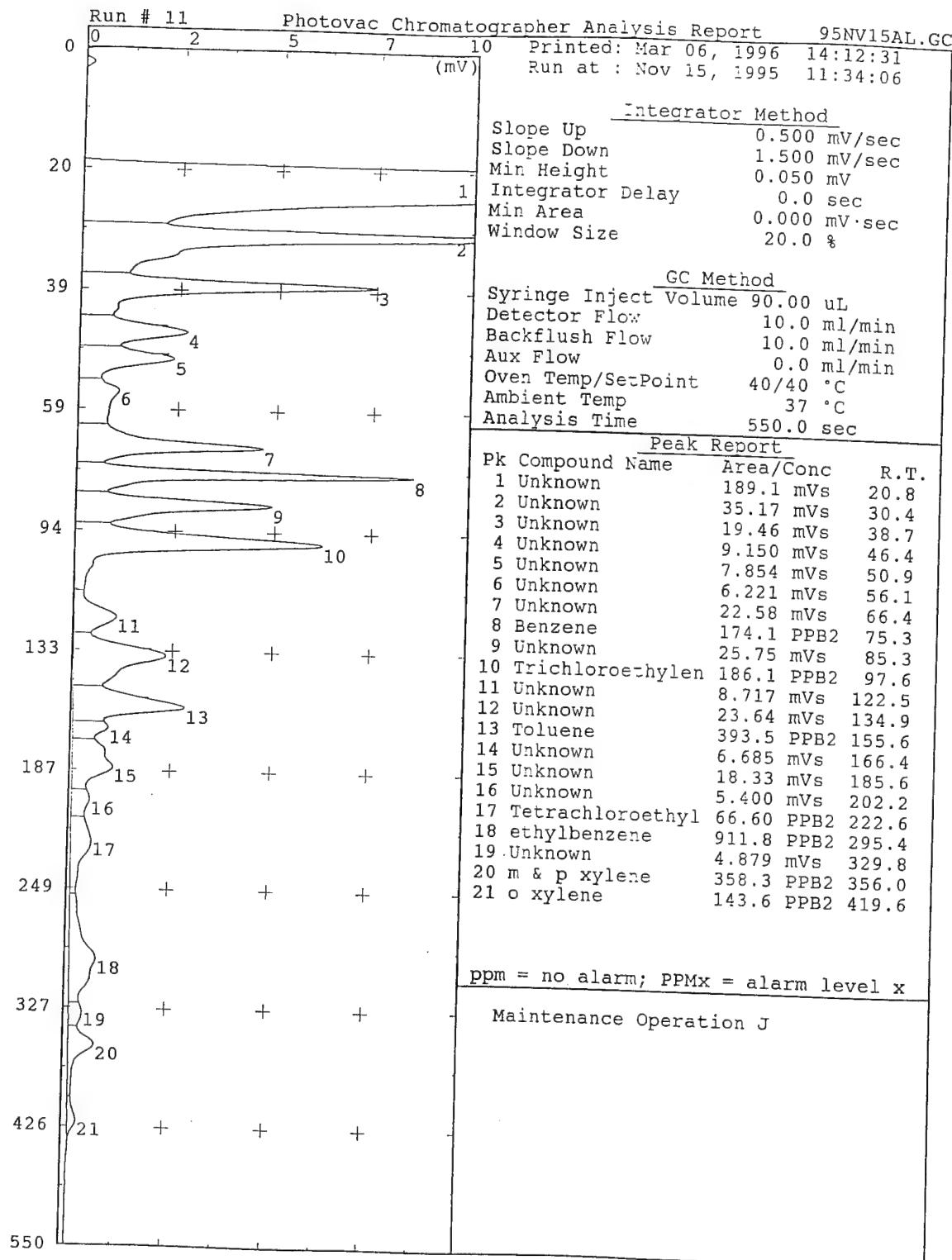


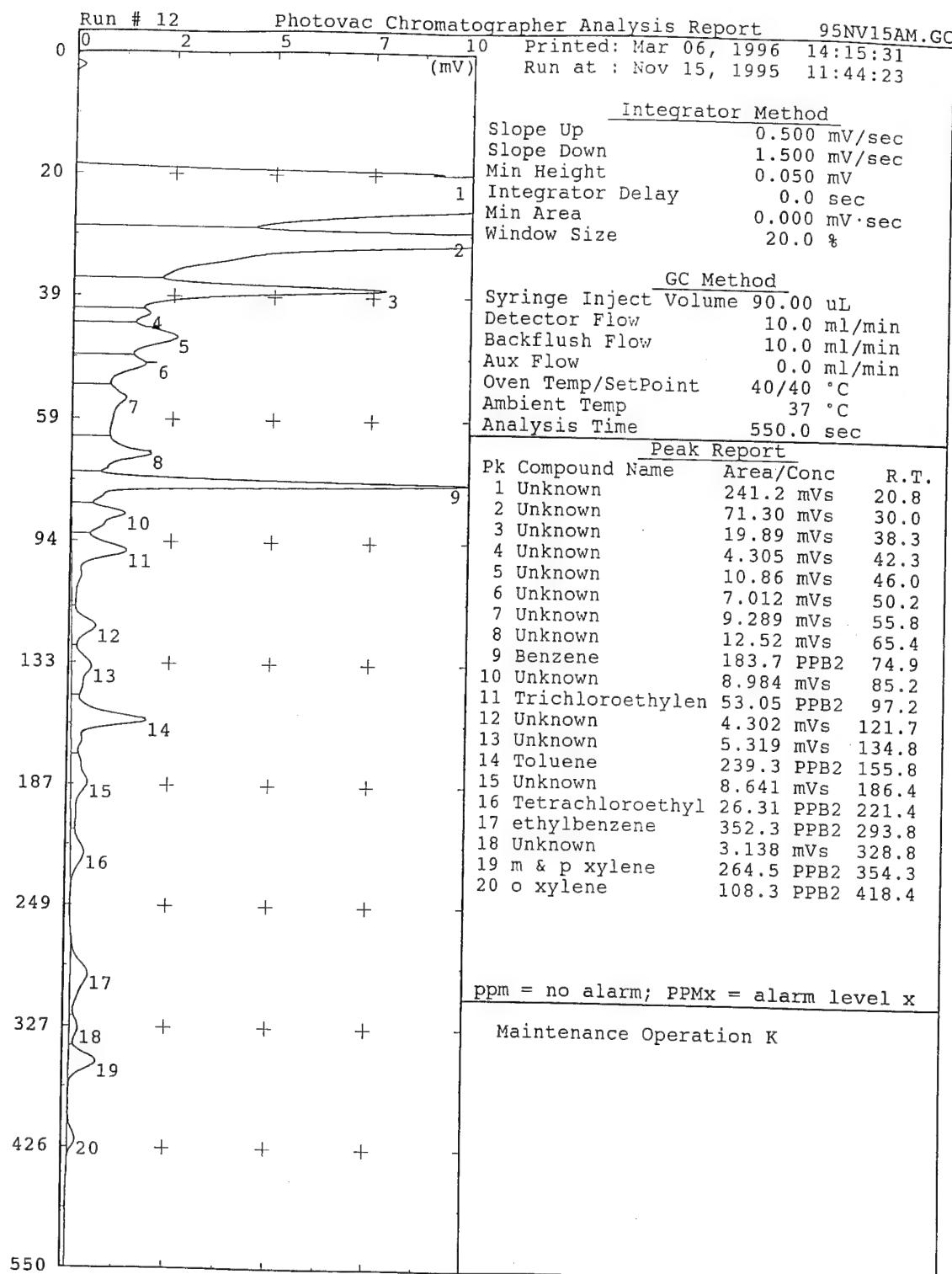


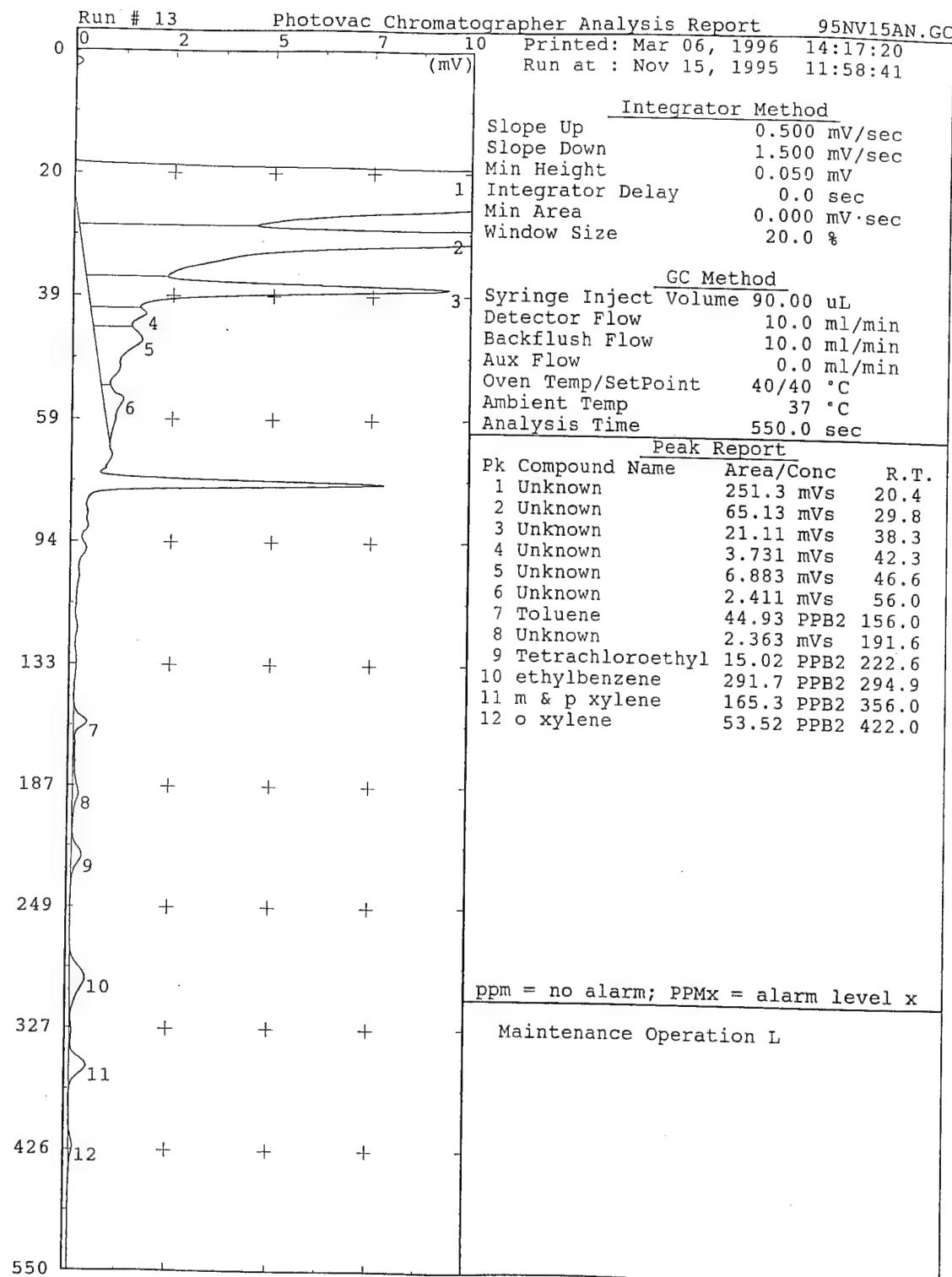


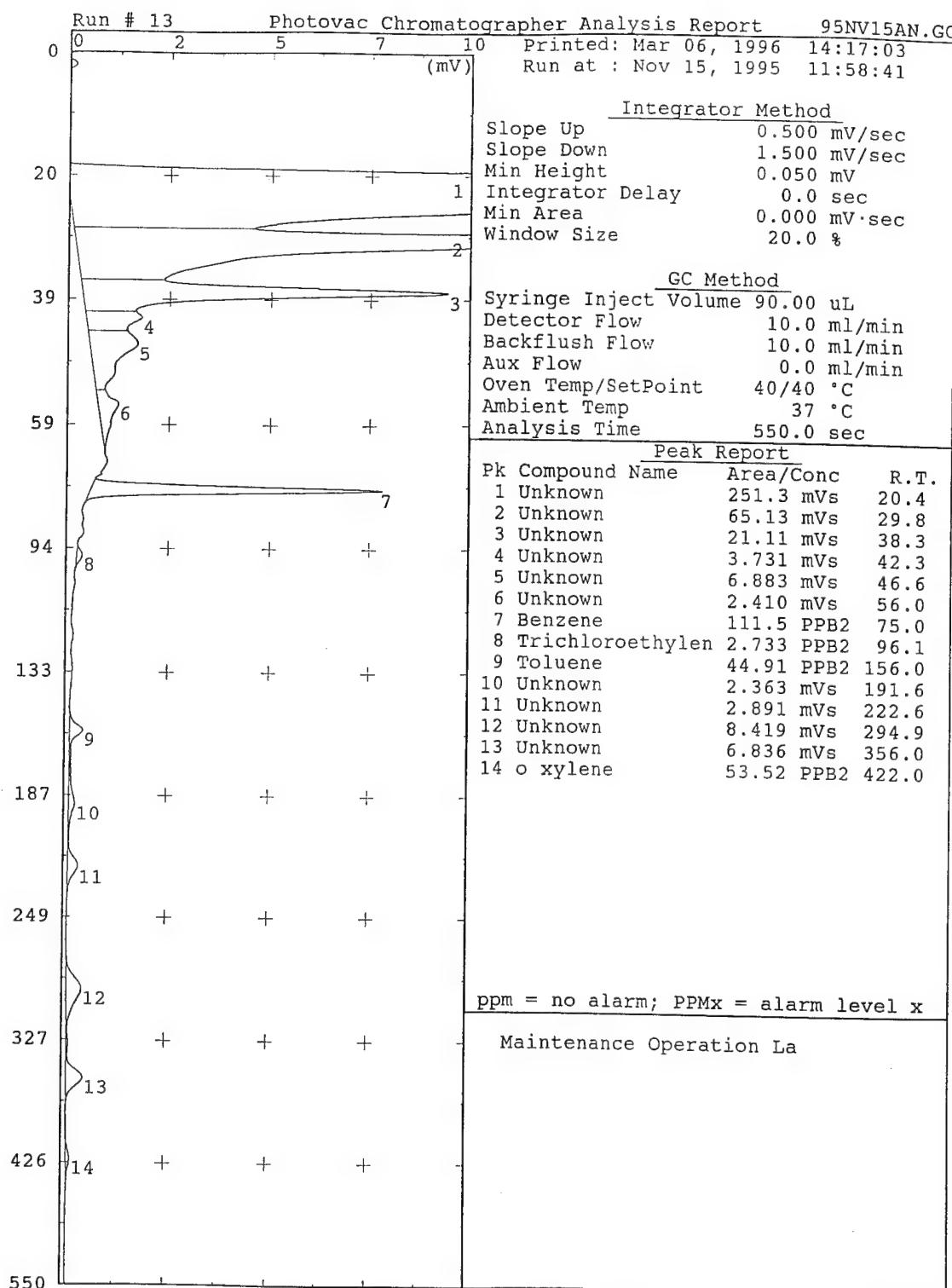


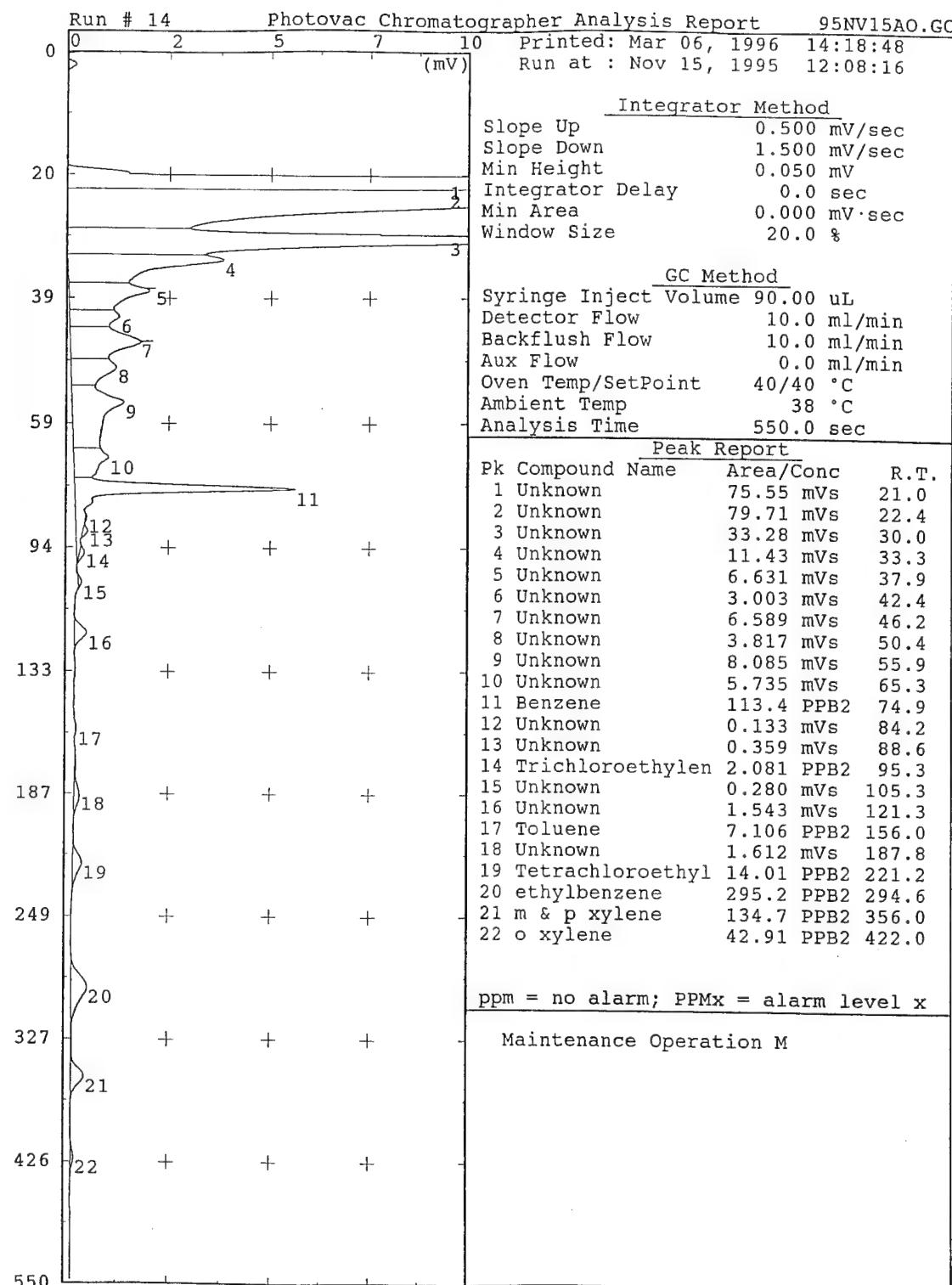


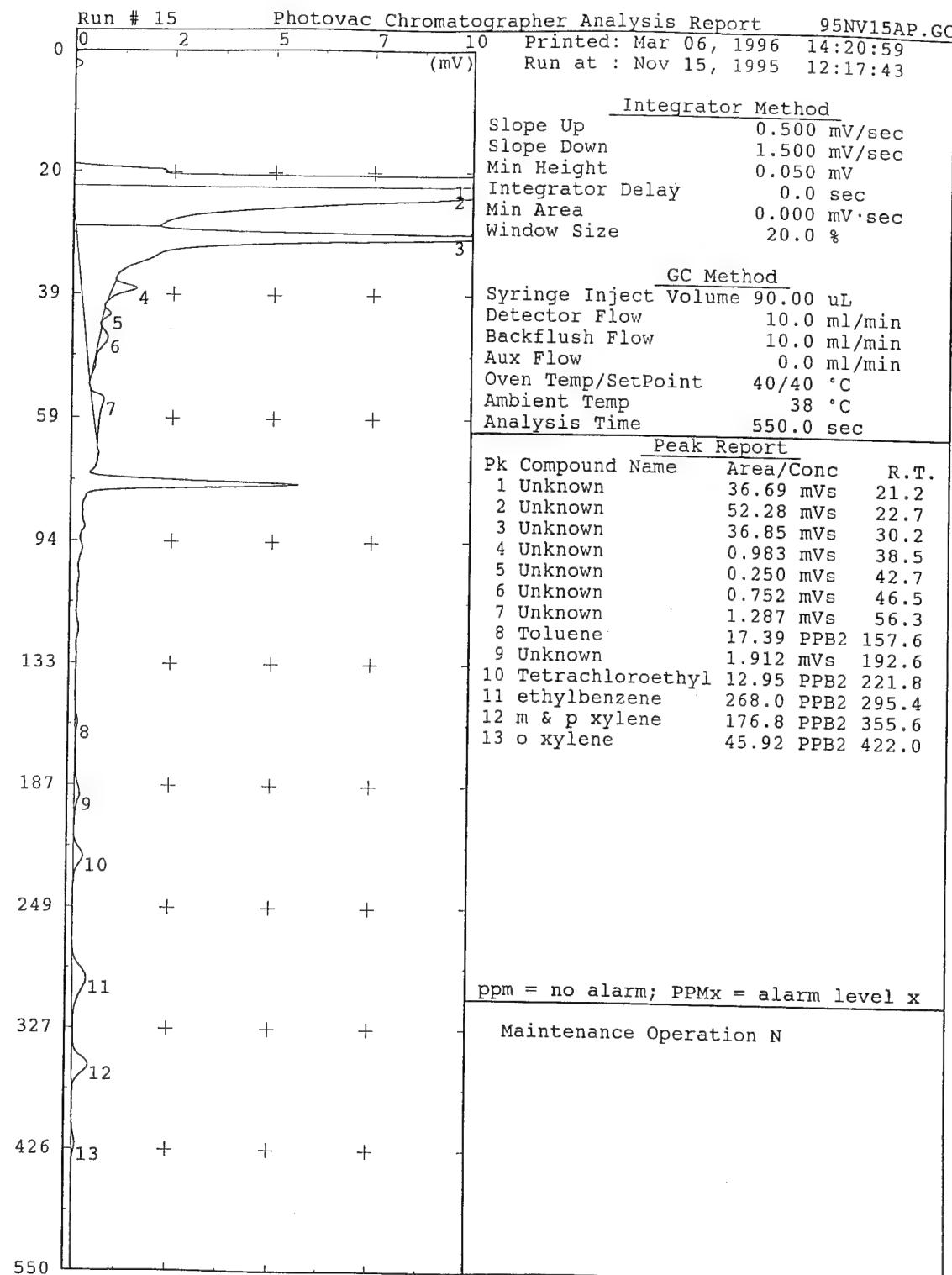


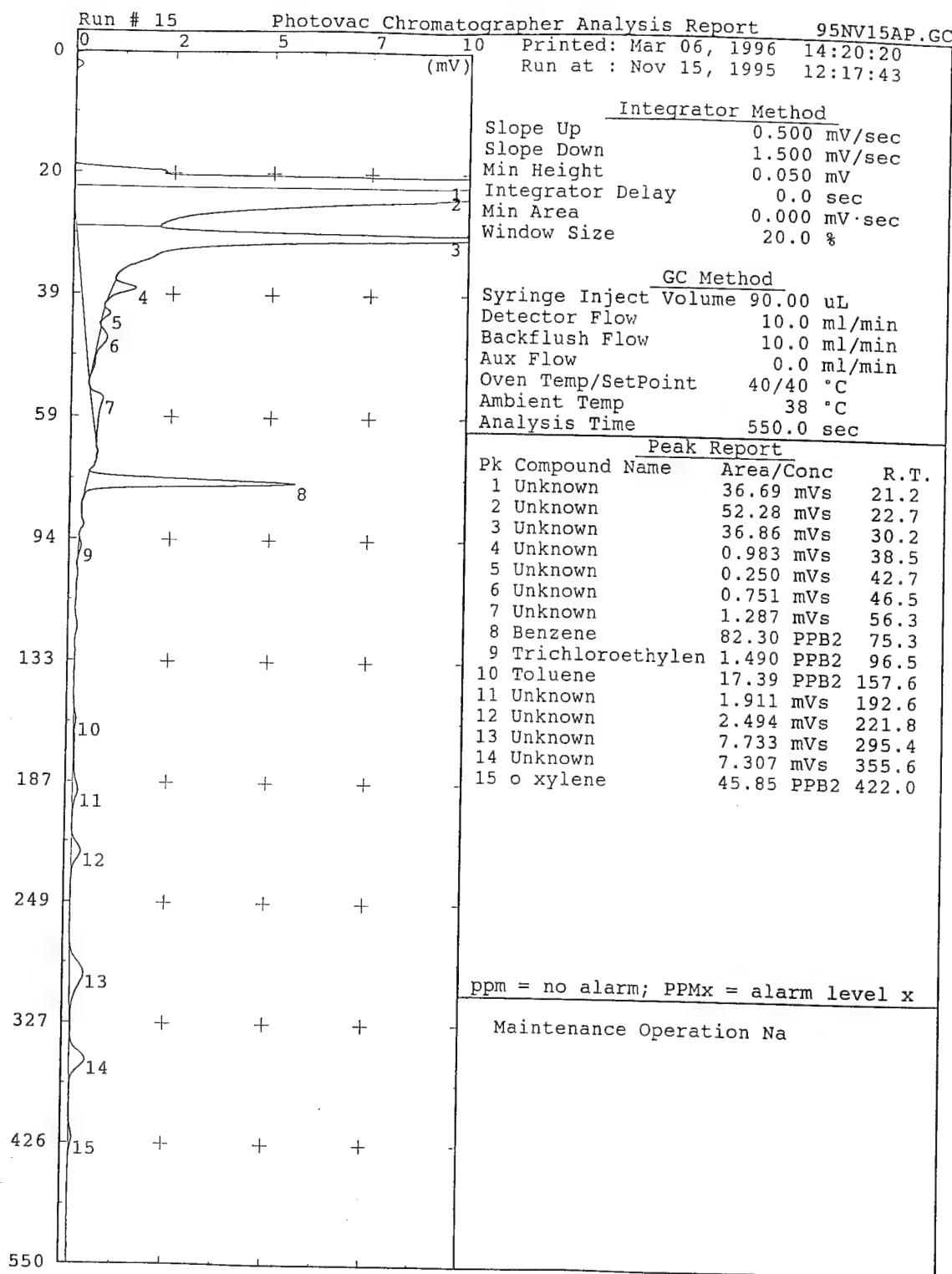


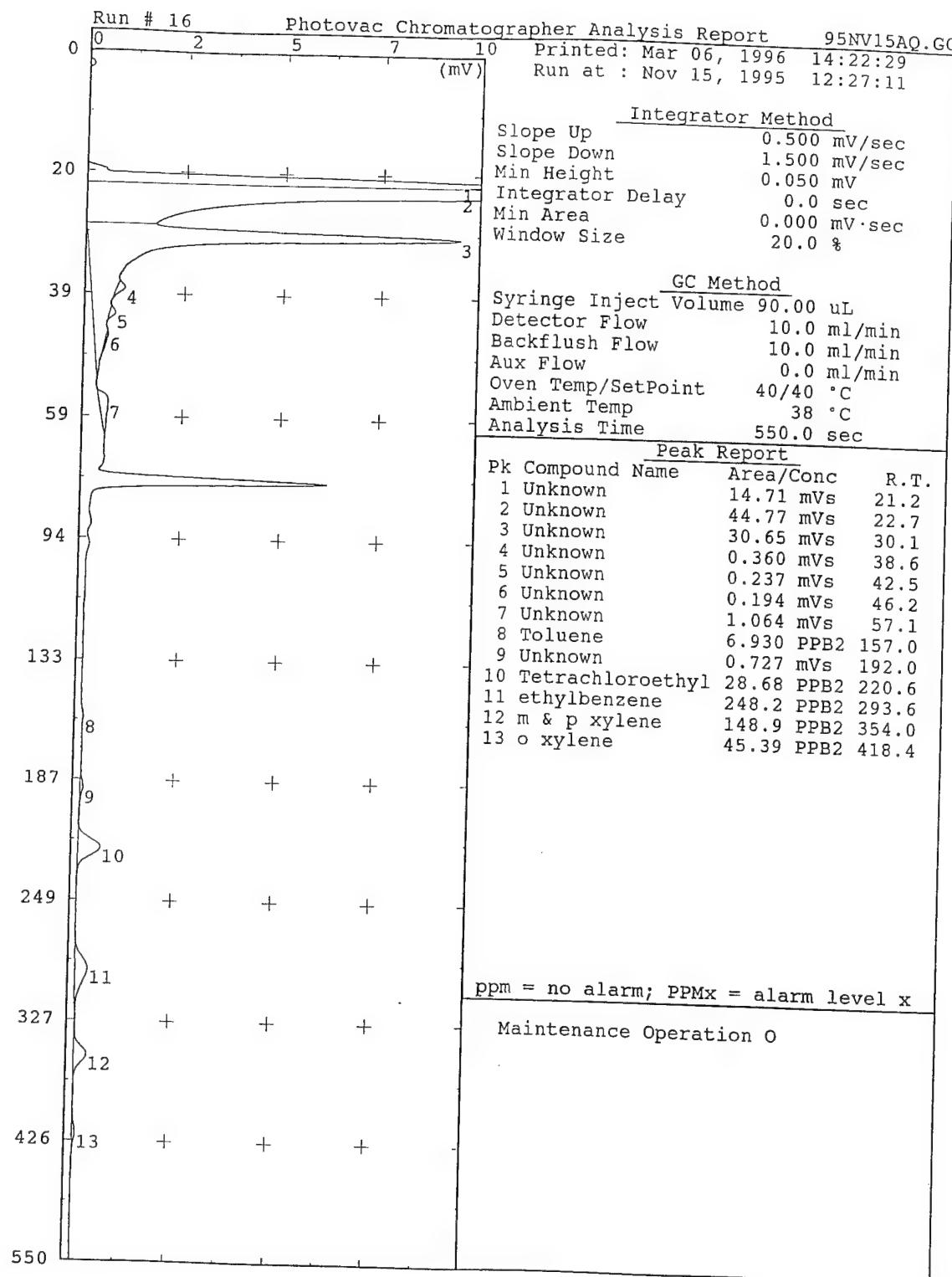


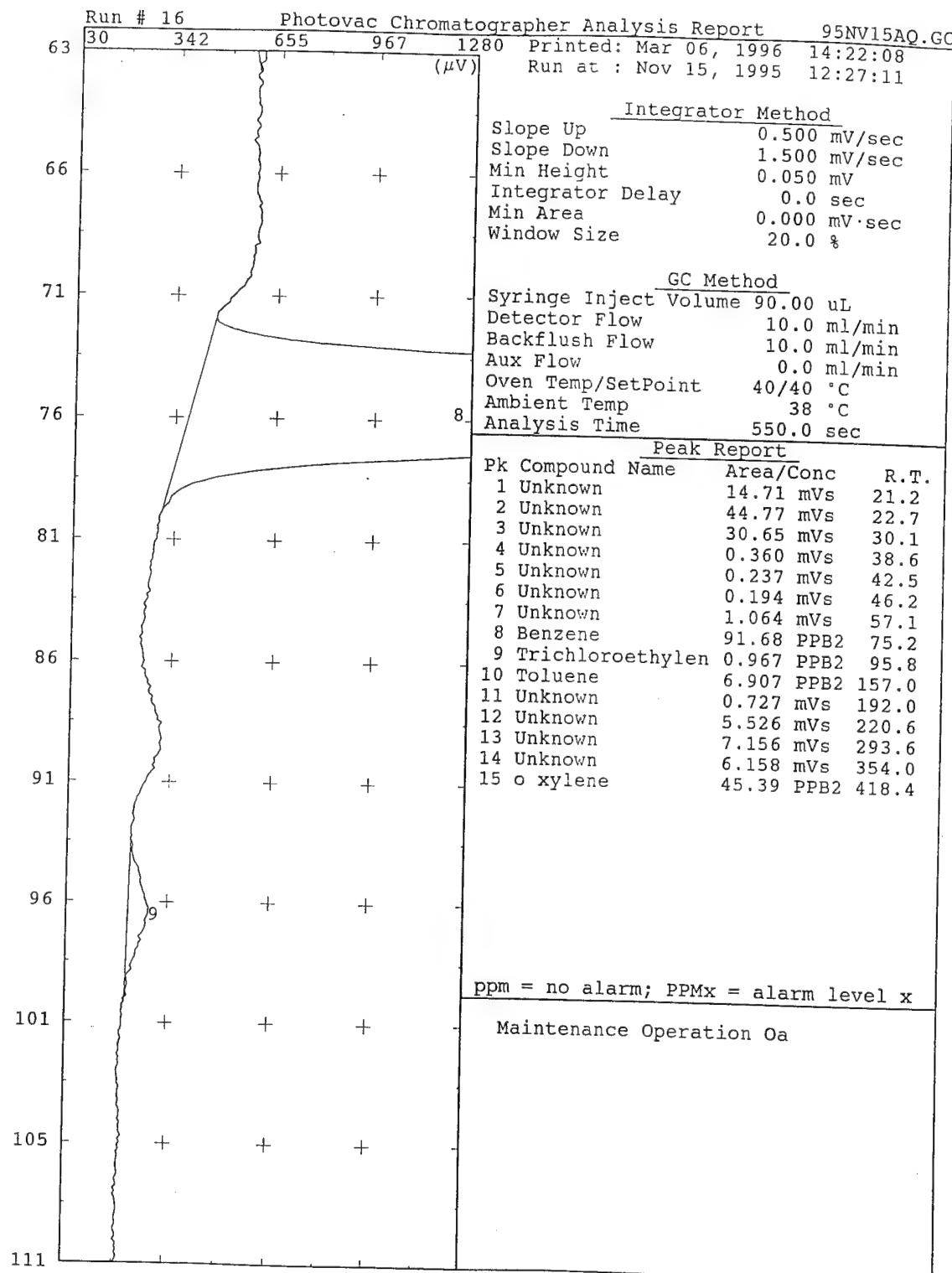


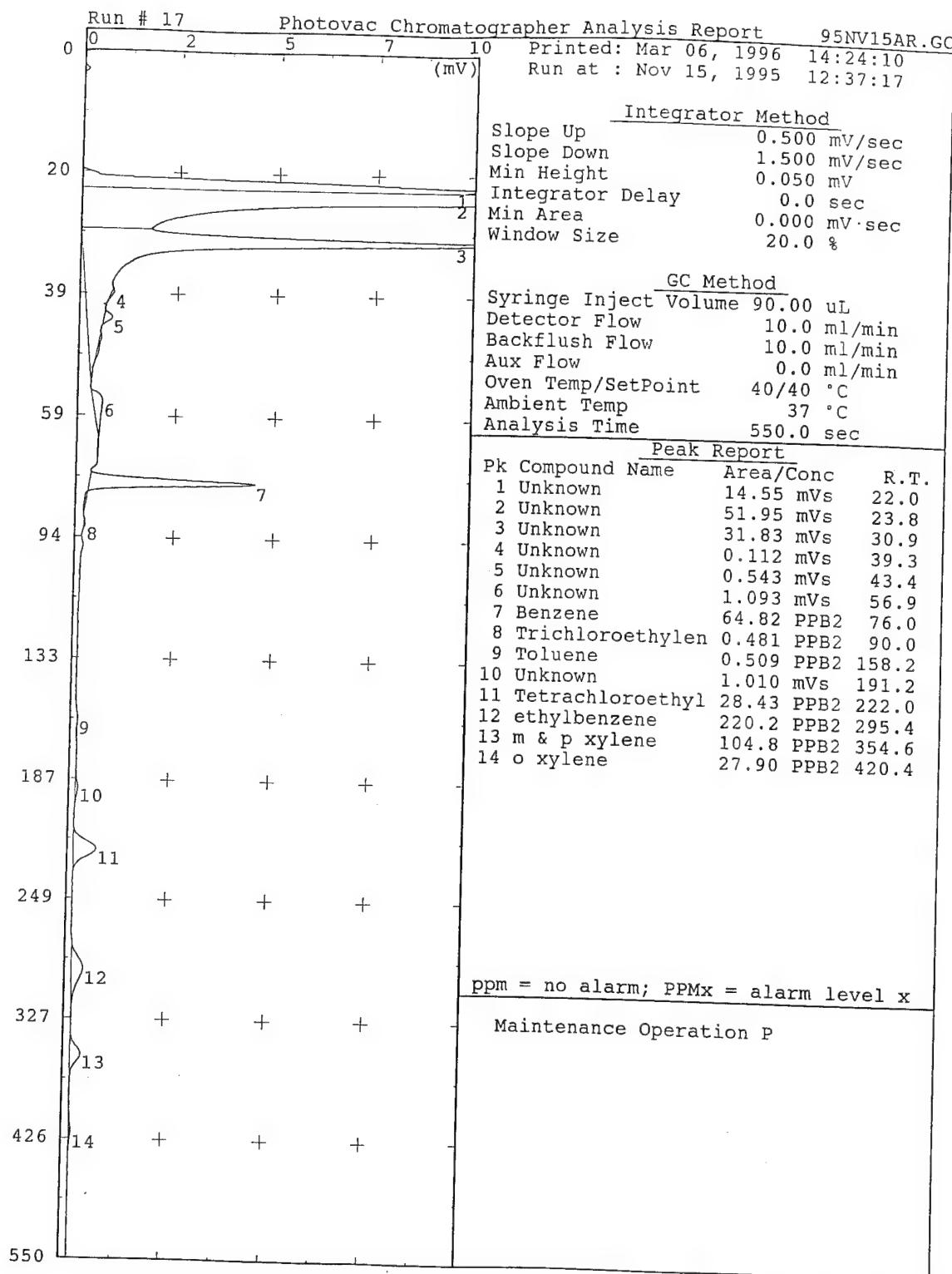






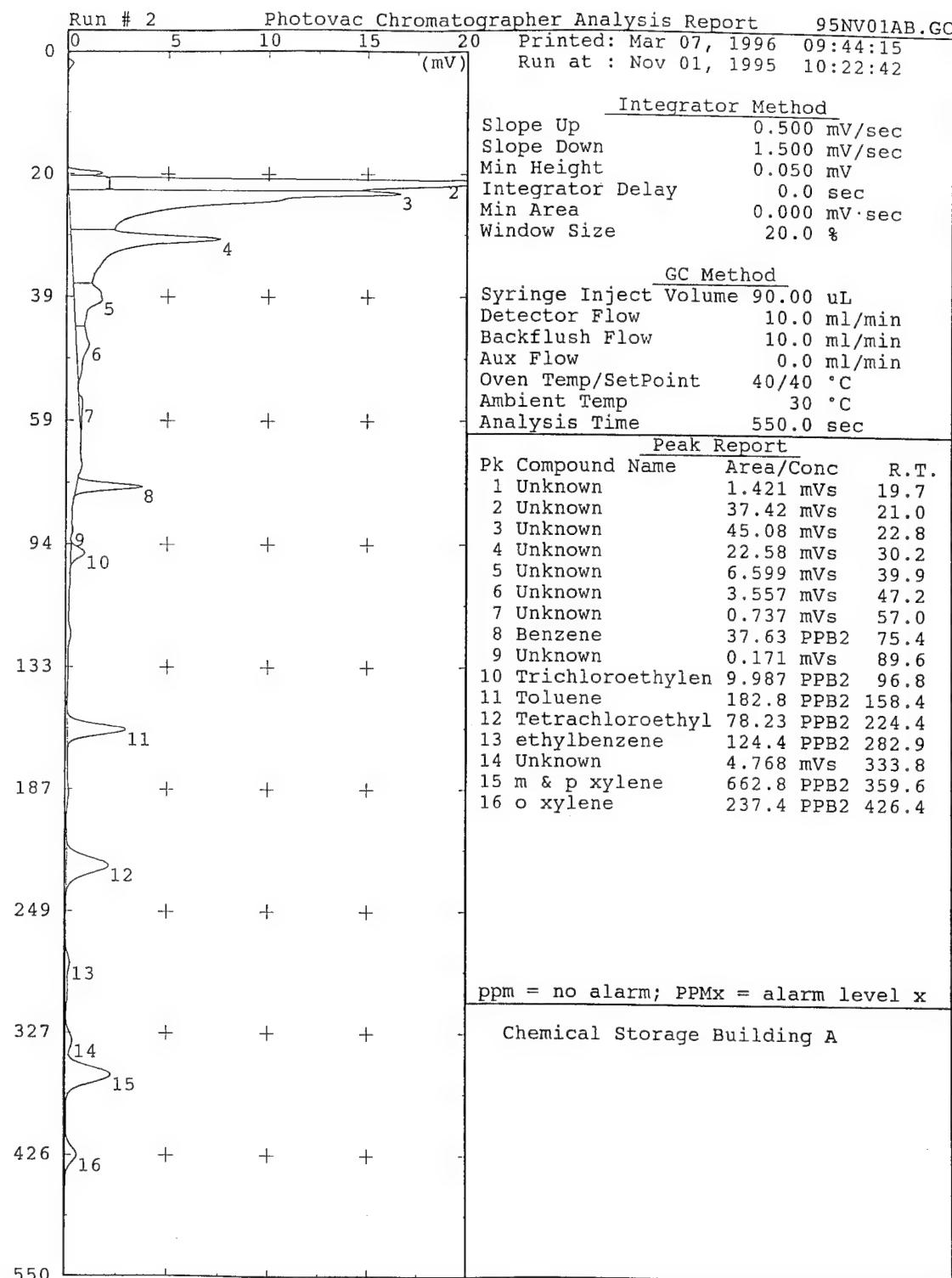


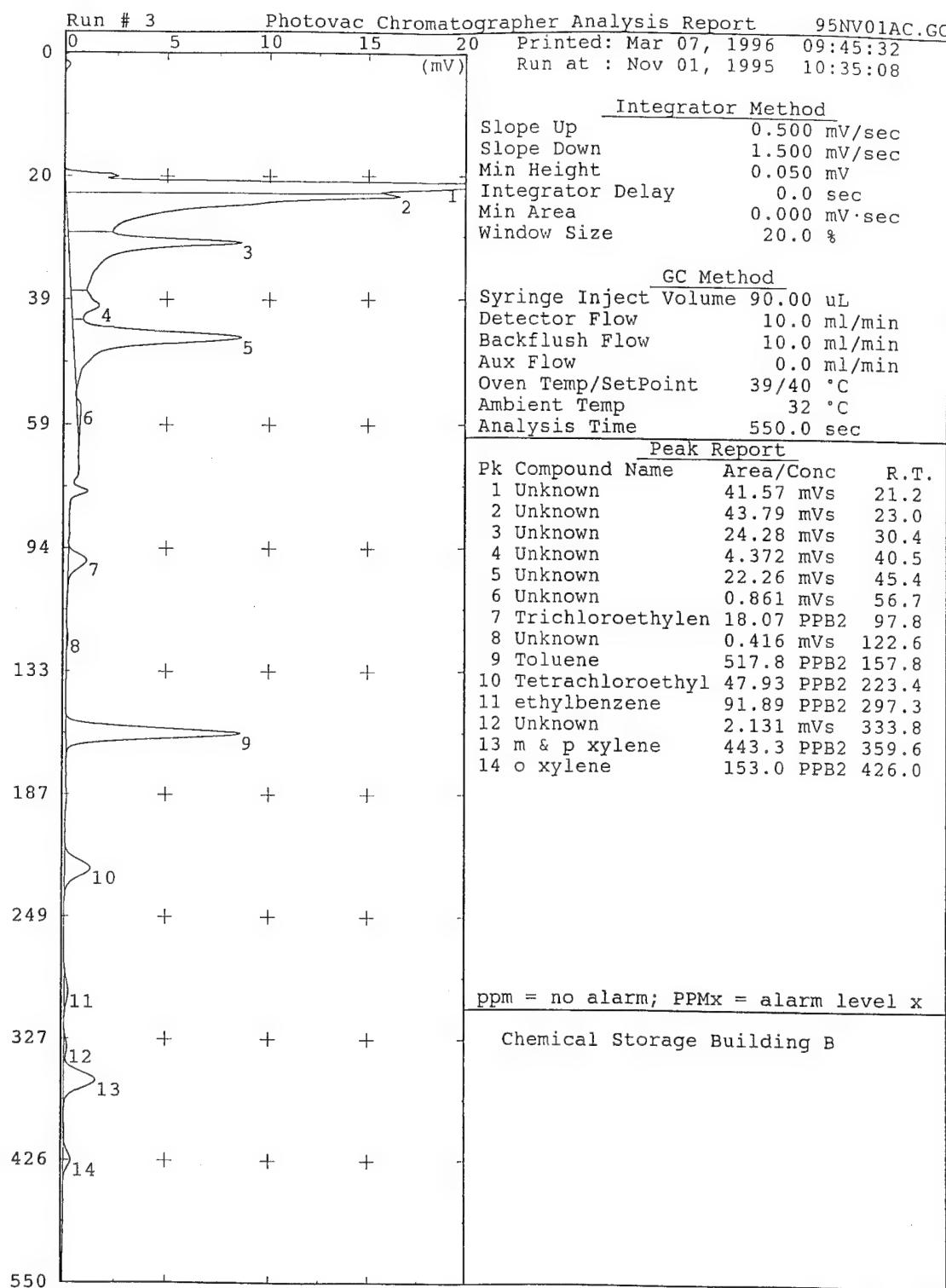


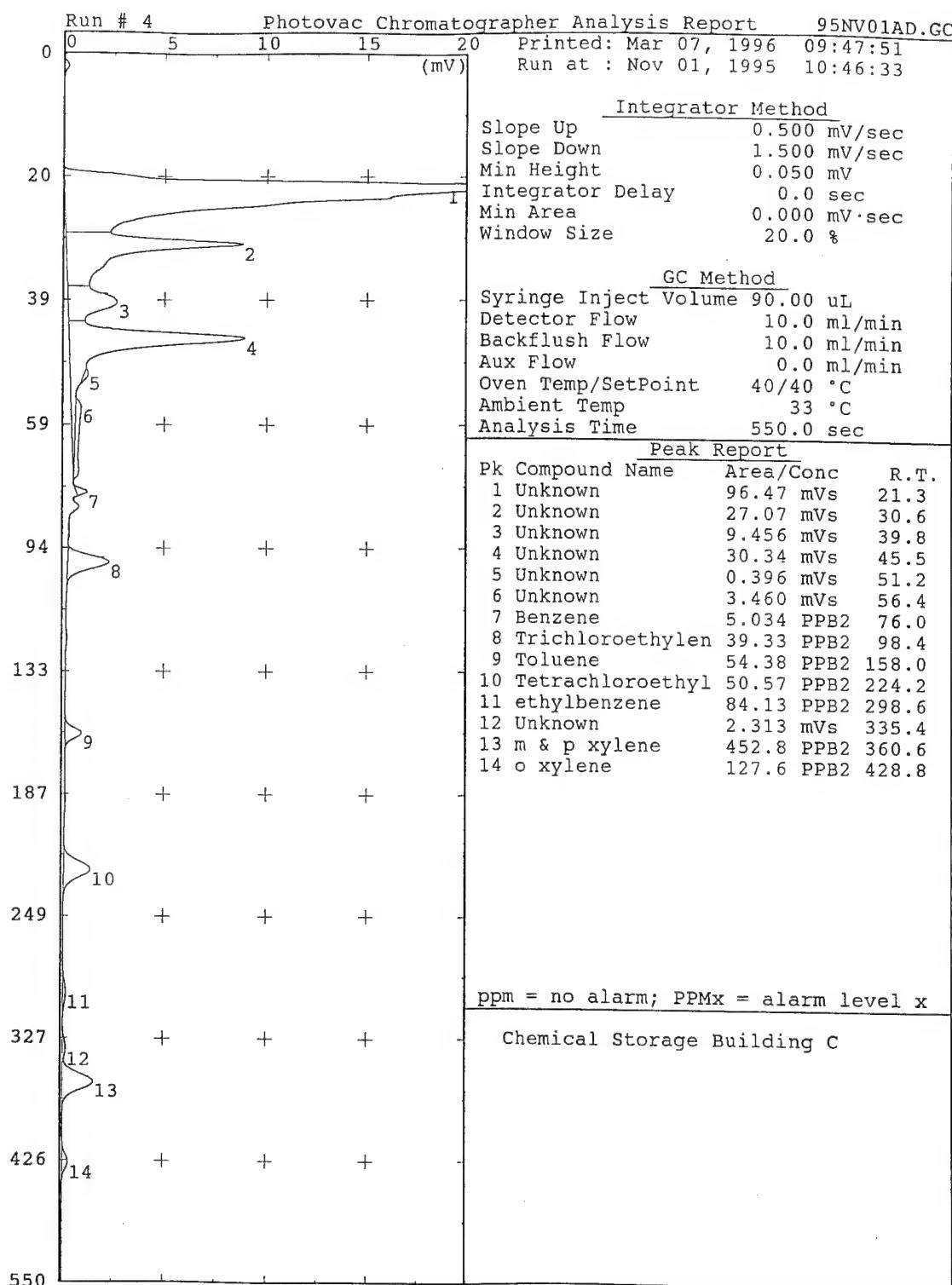


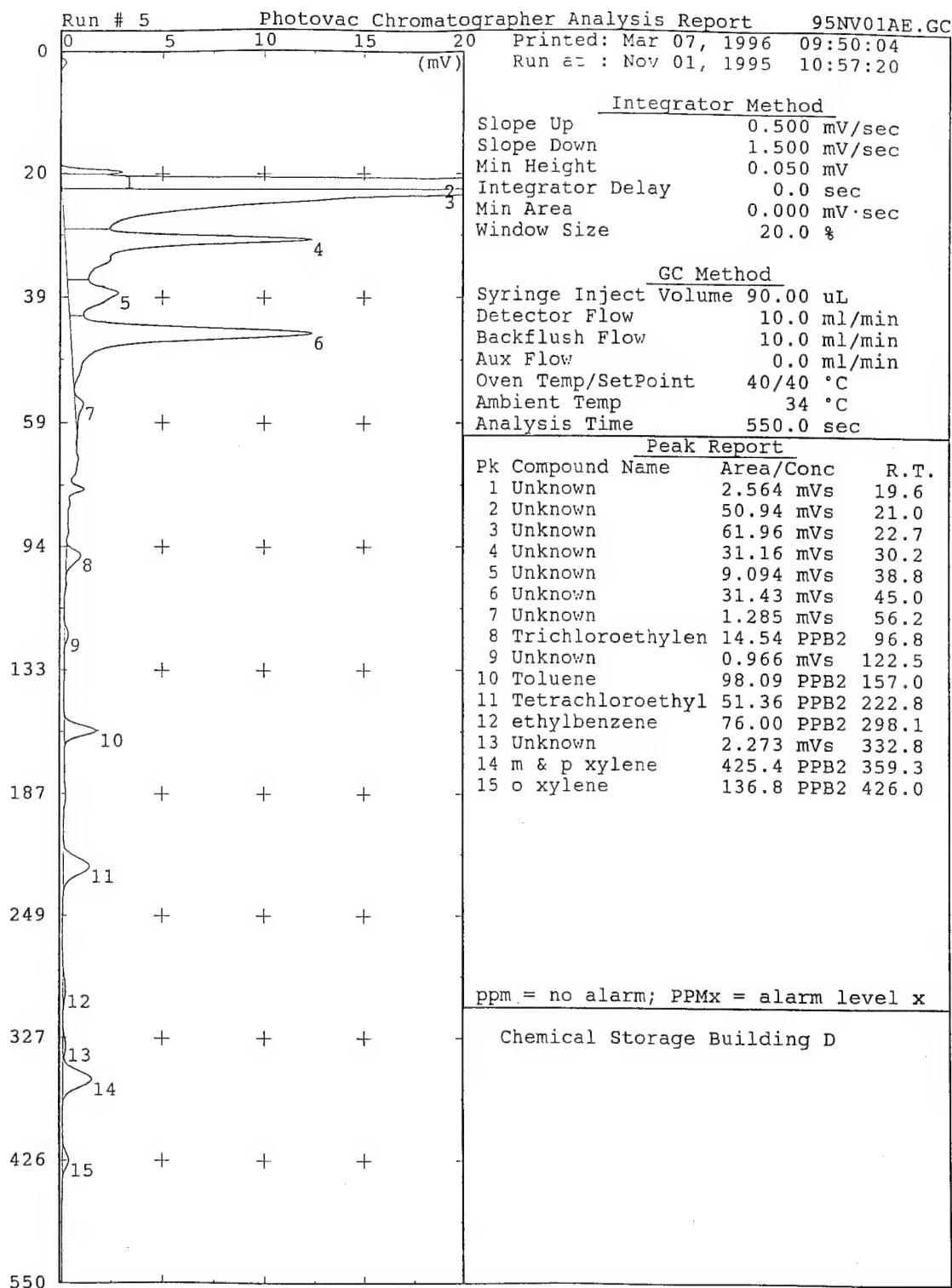
**APPENDIX E**

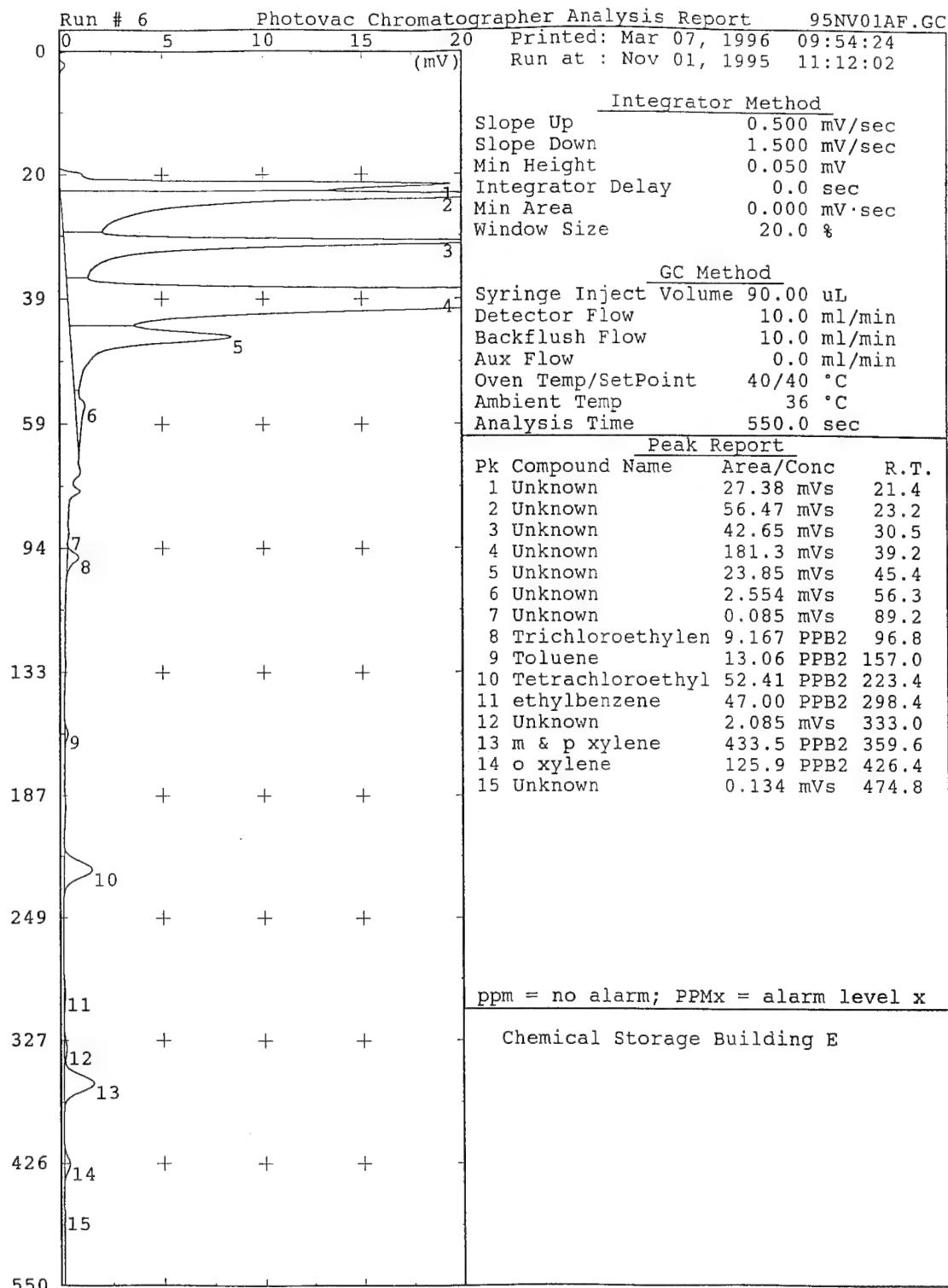
**CHEMICAL STORAGE BUILDING CHROMATOGRAMS**

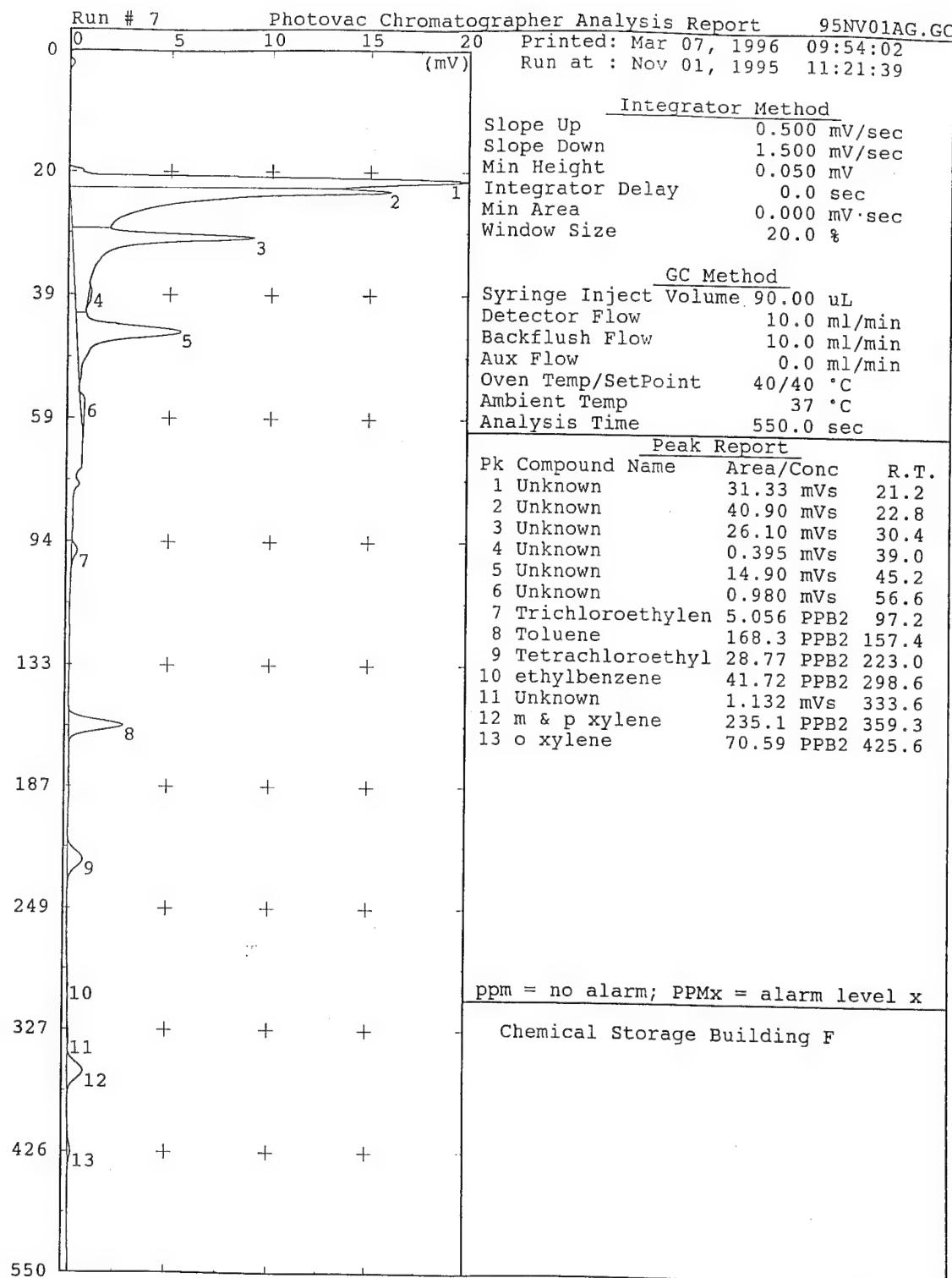


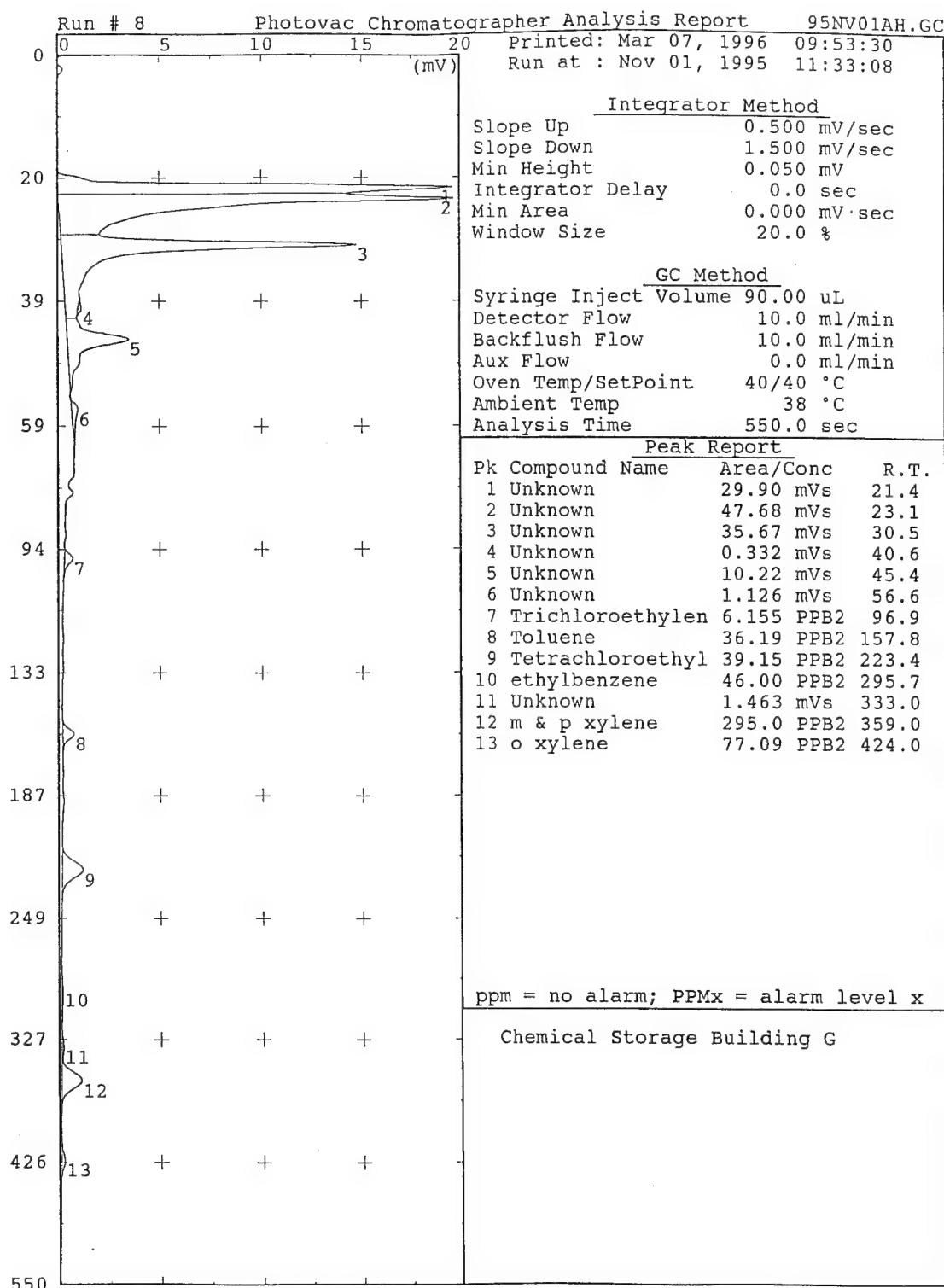


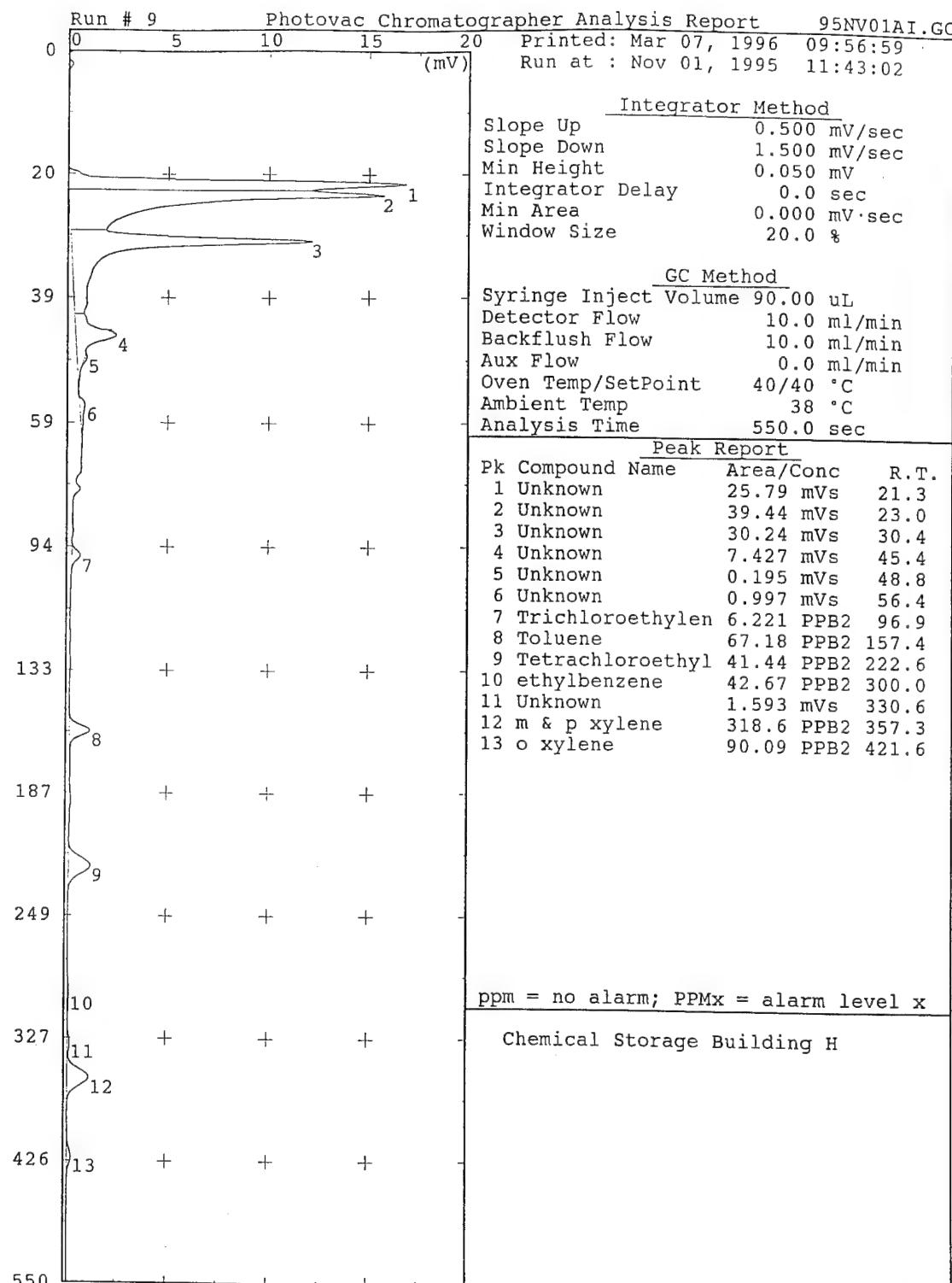


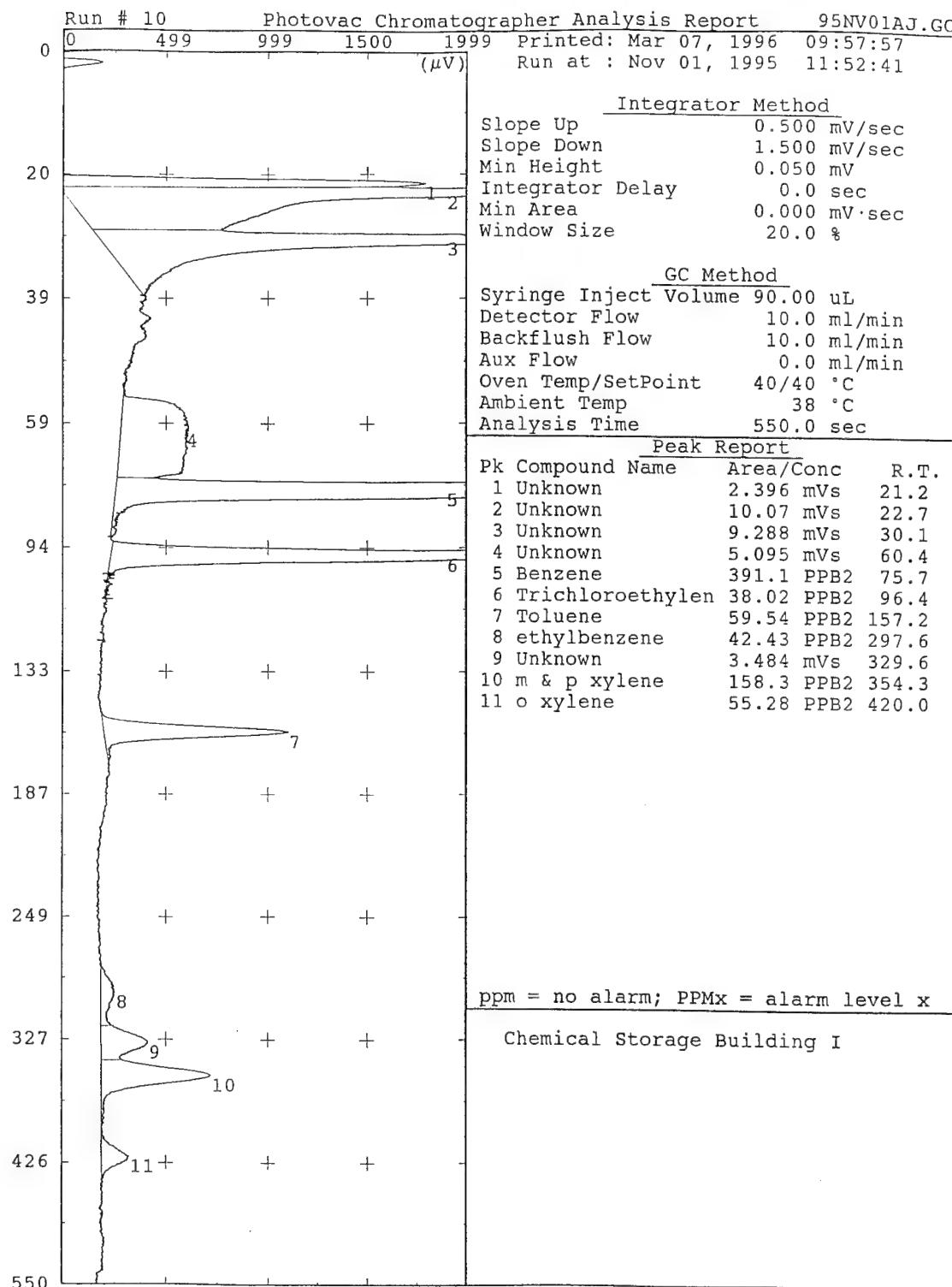


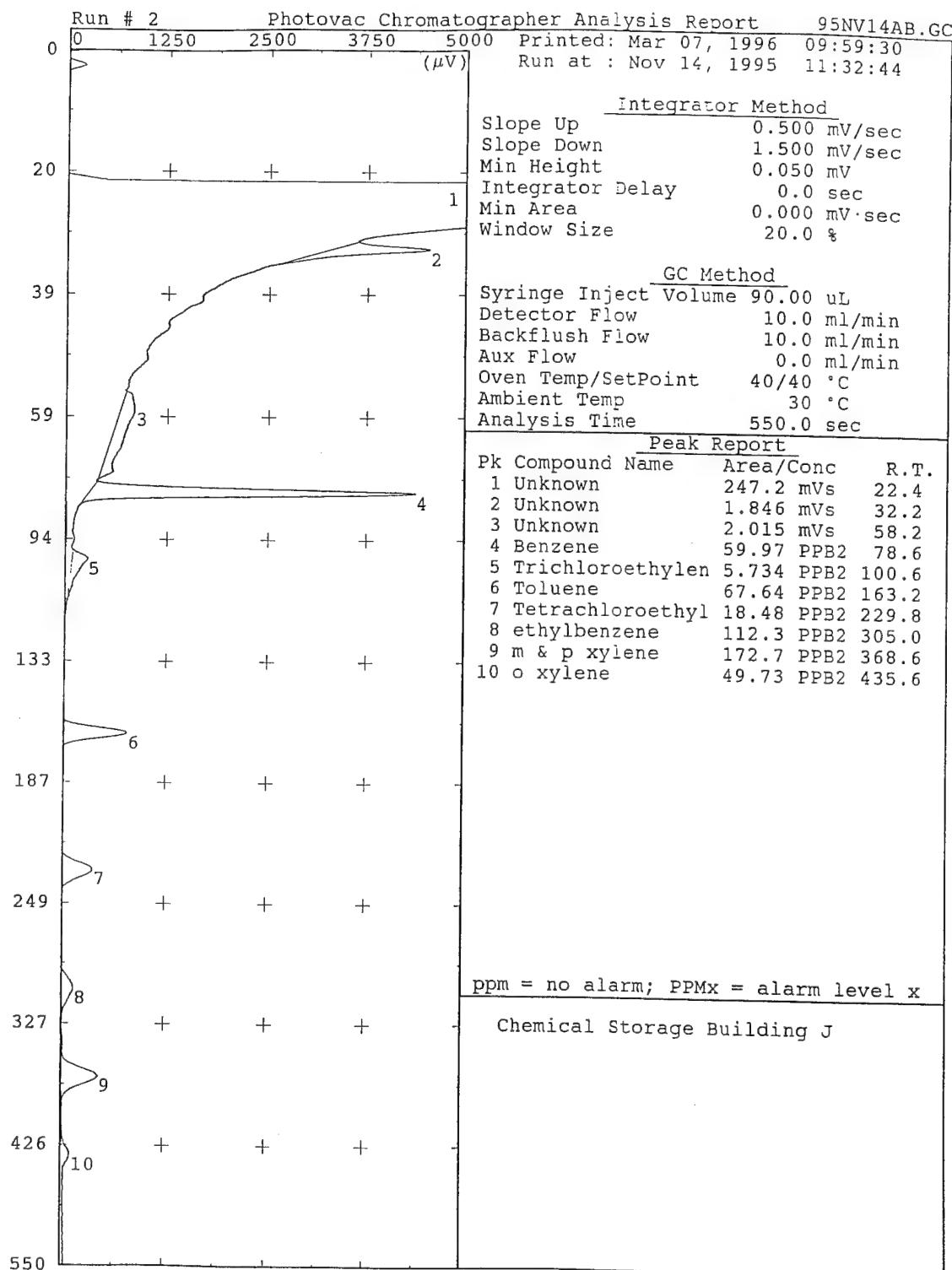


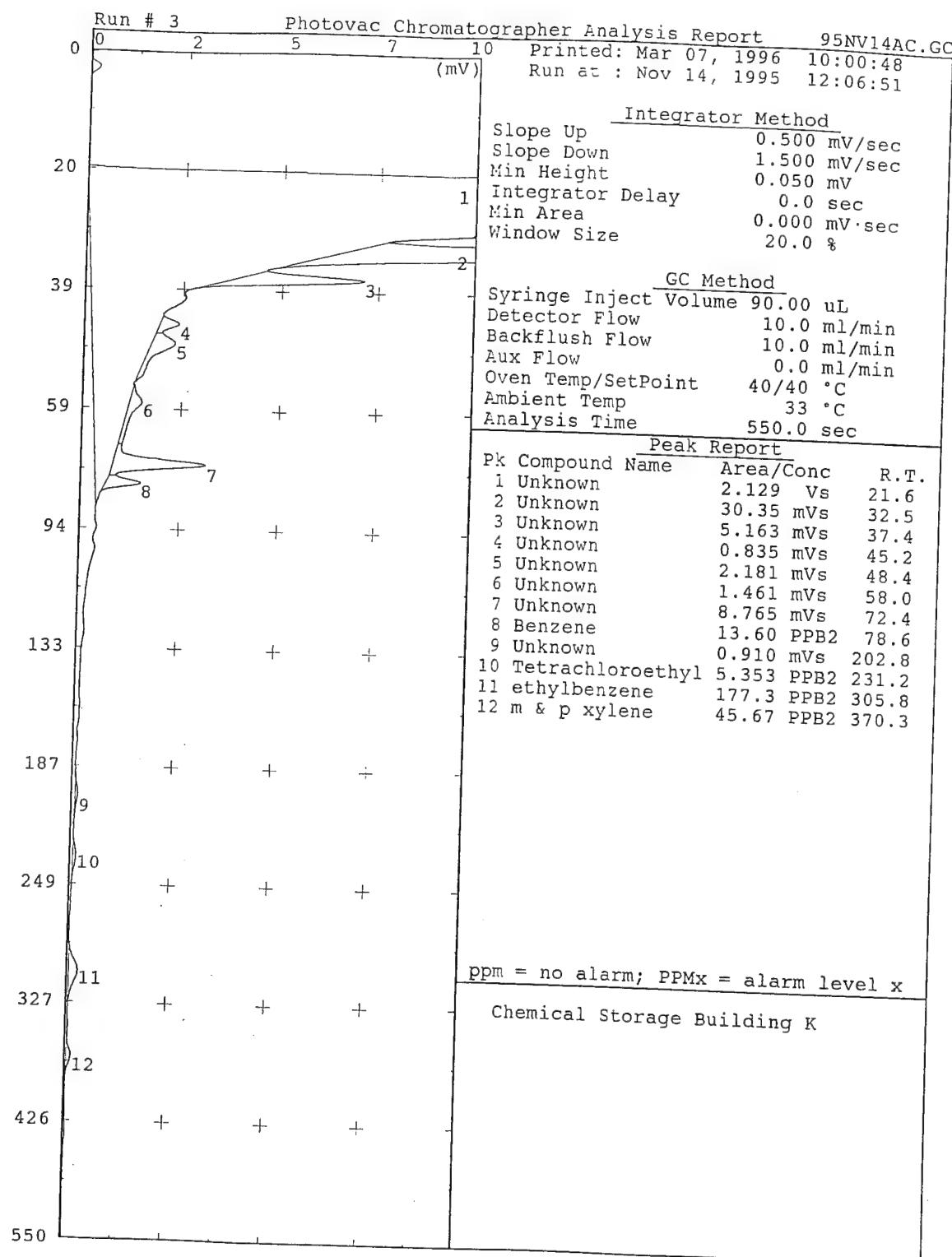


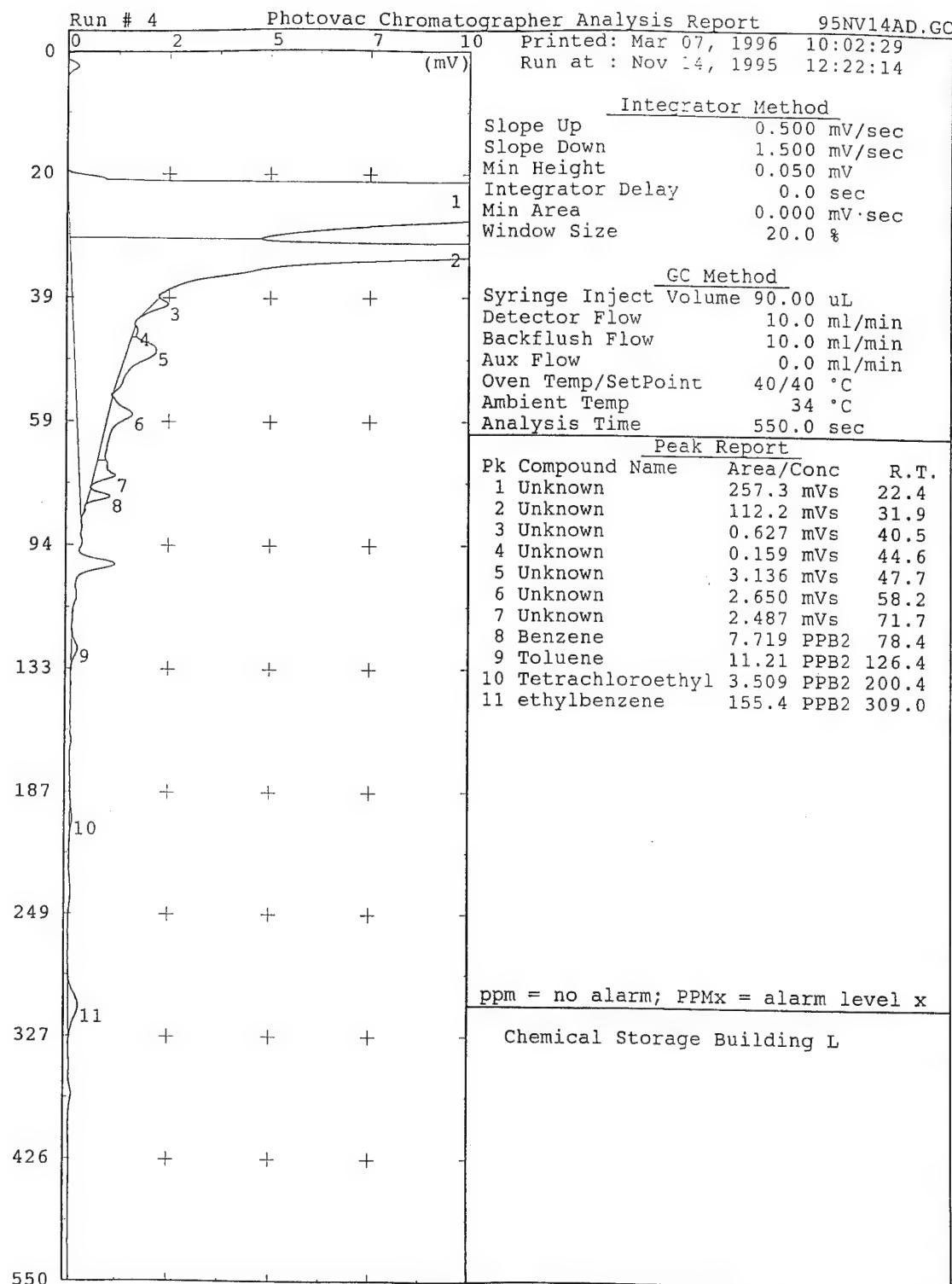


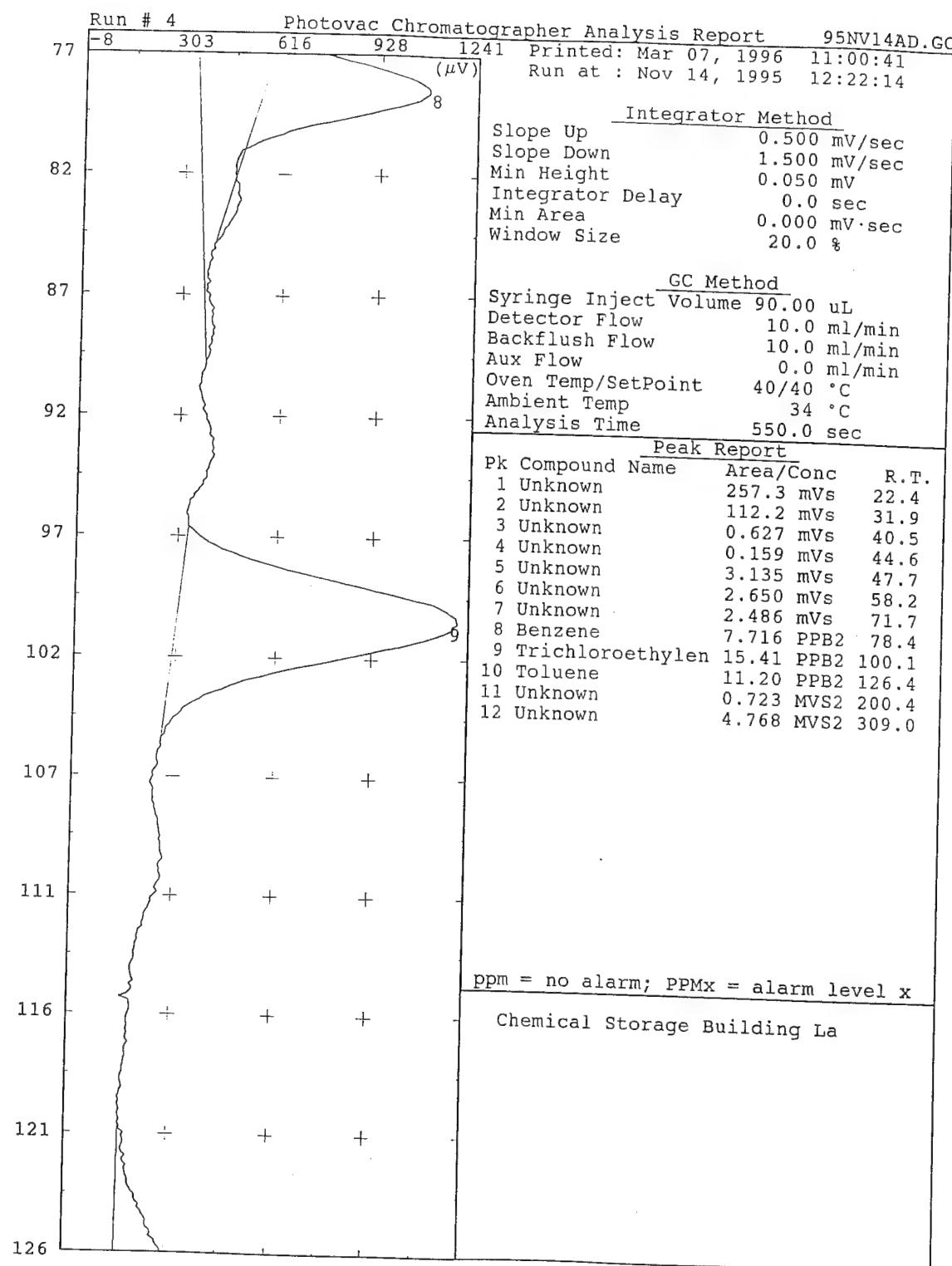


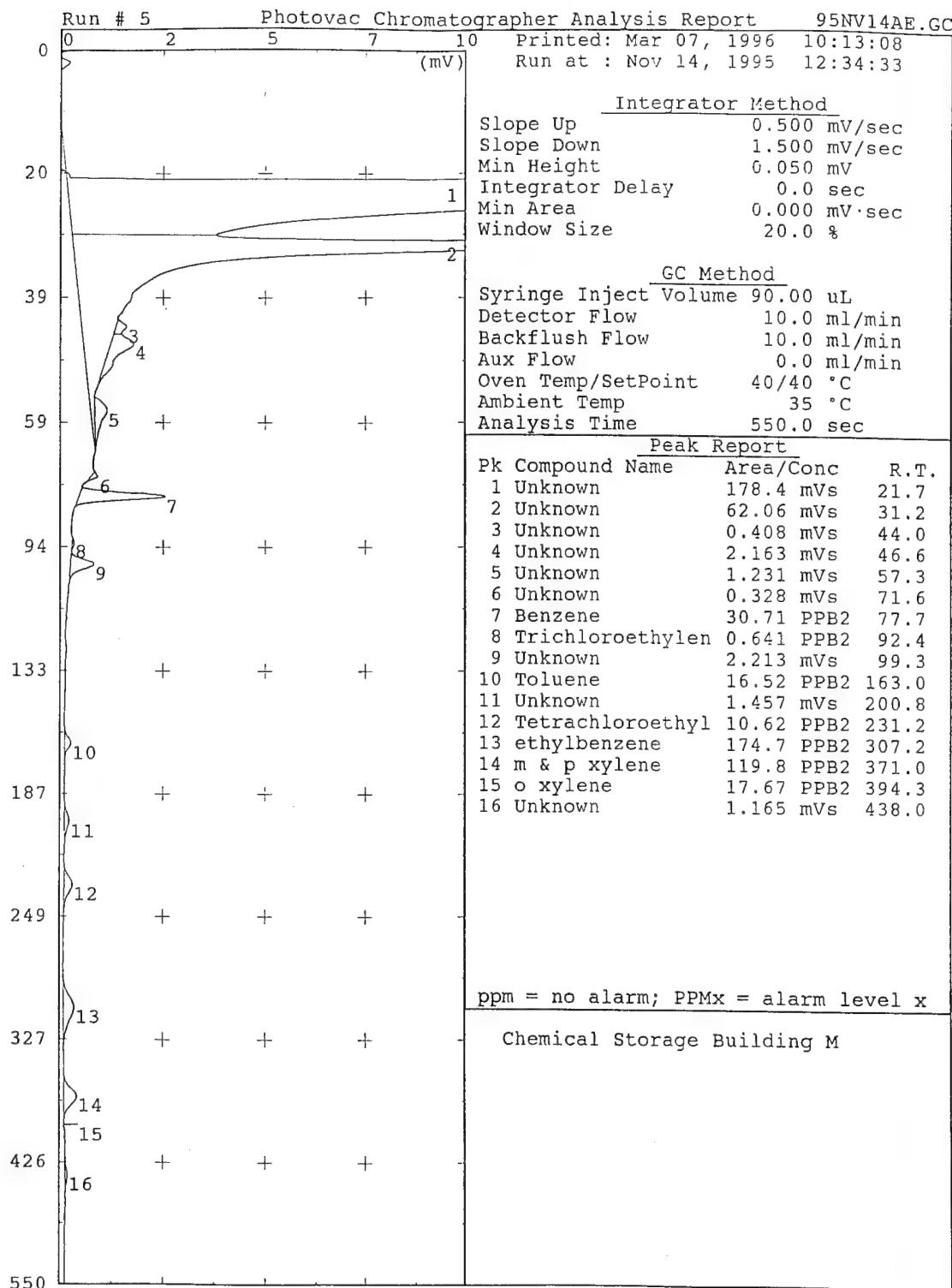


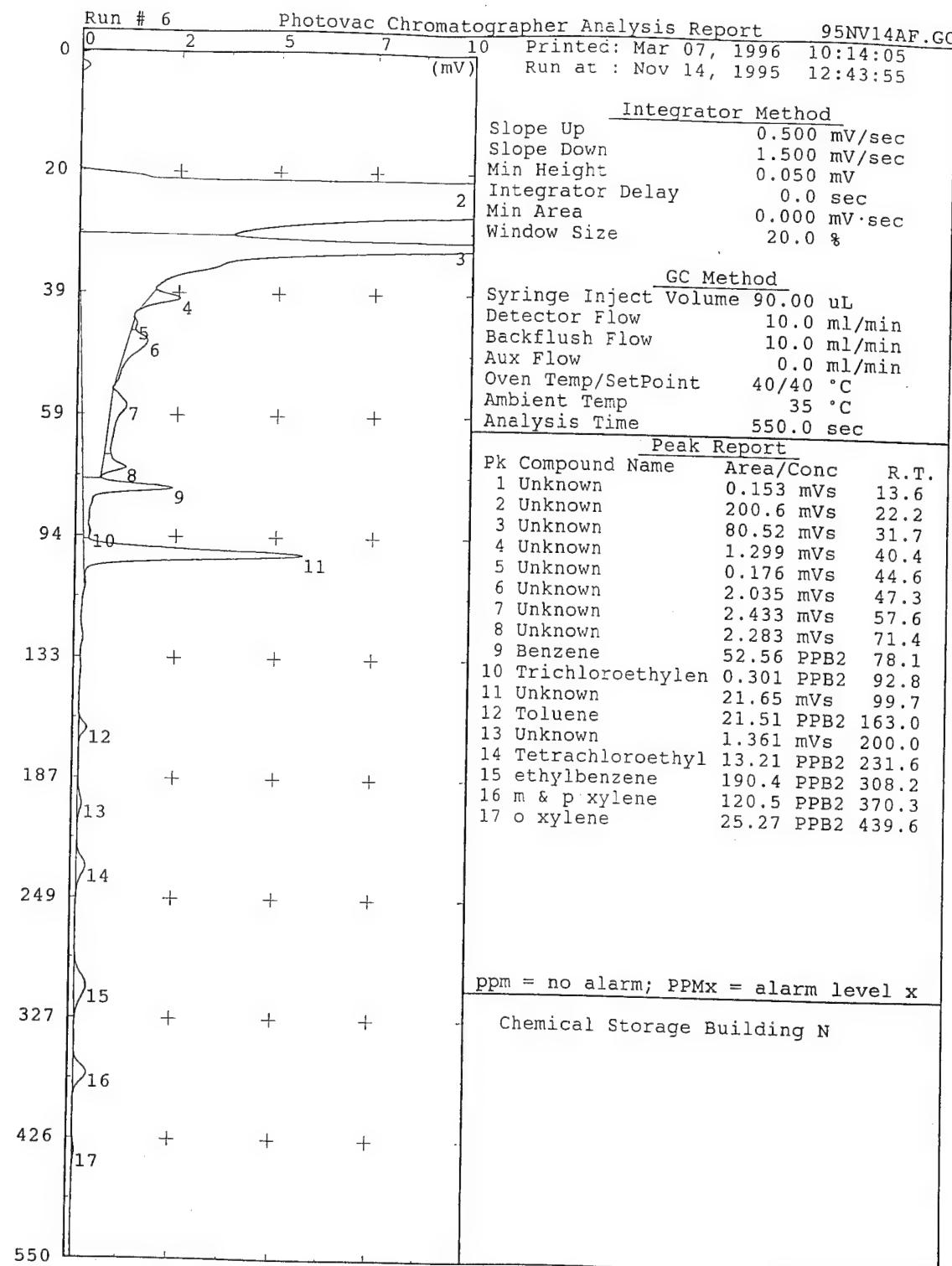


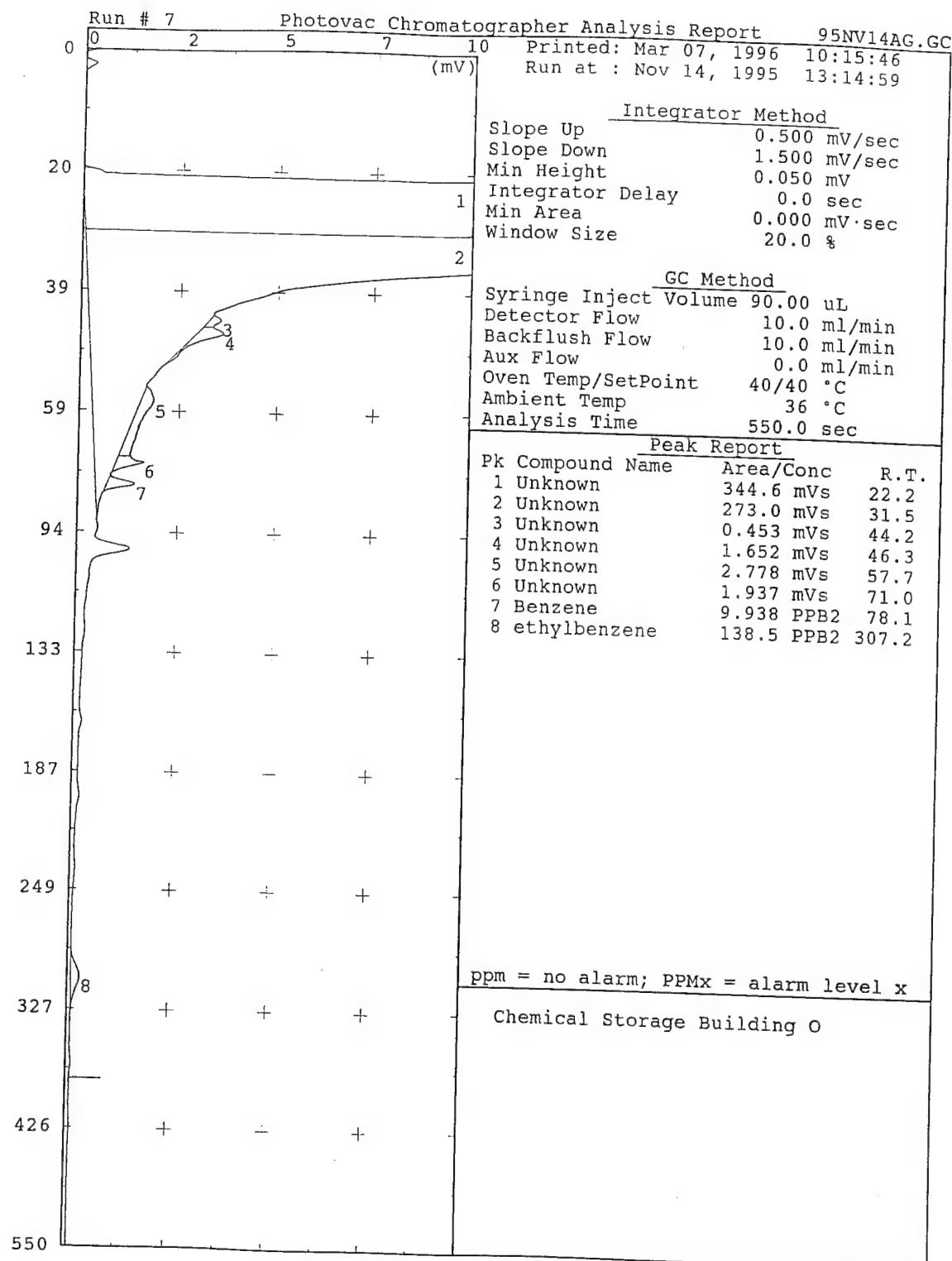


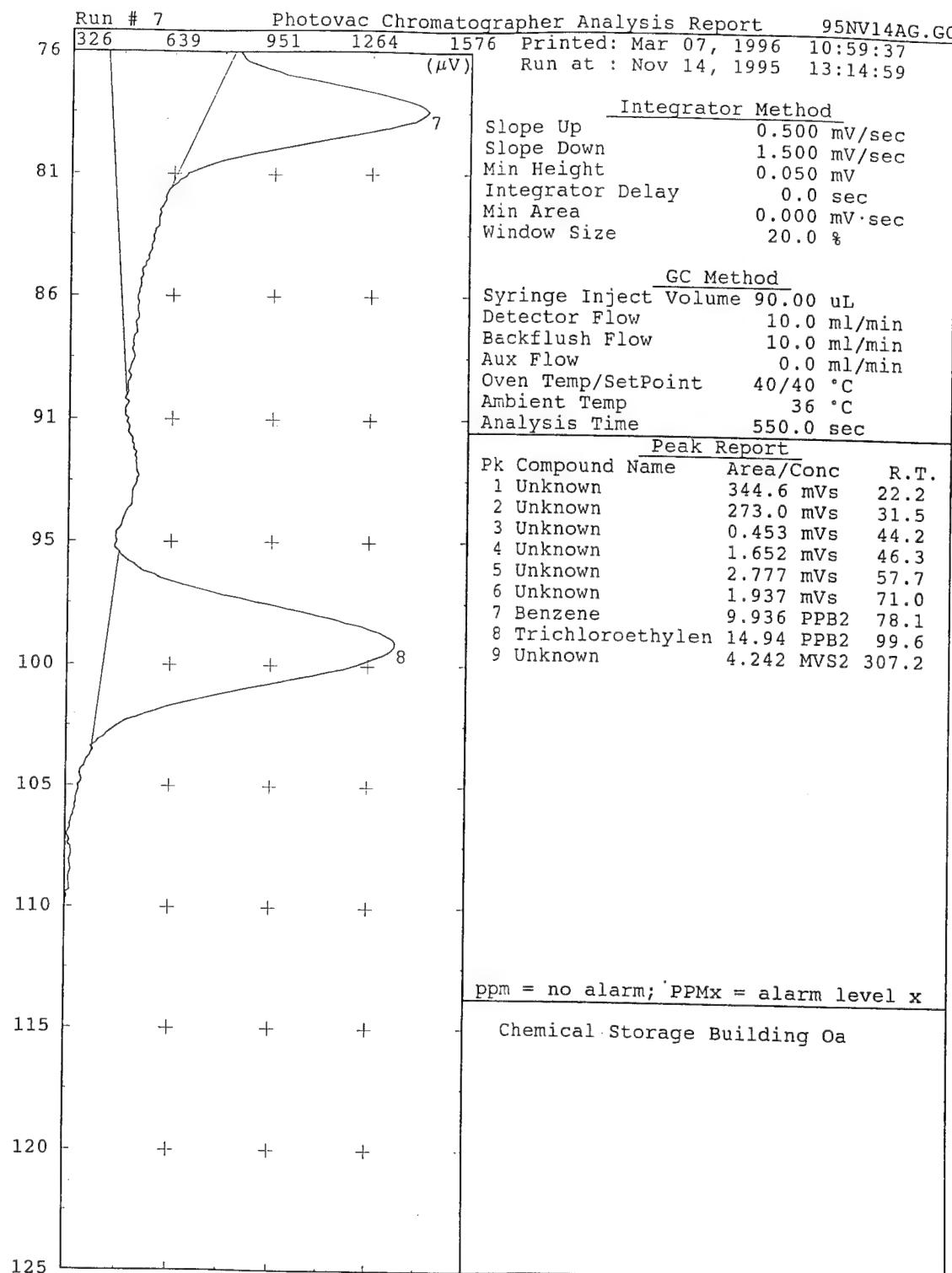


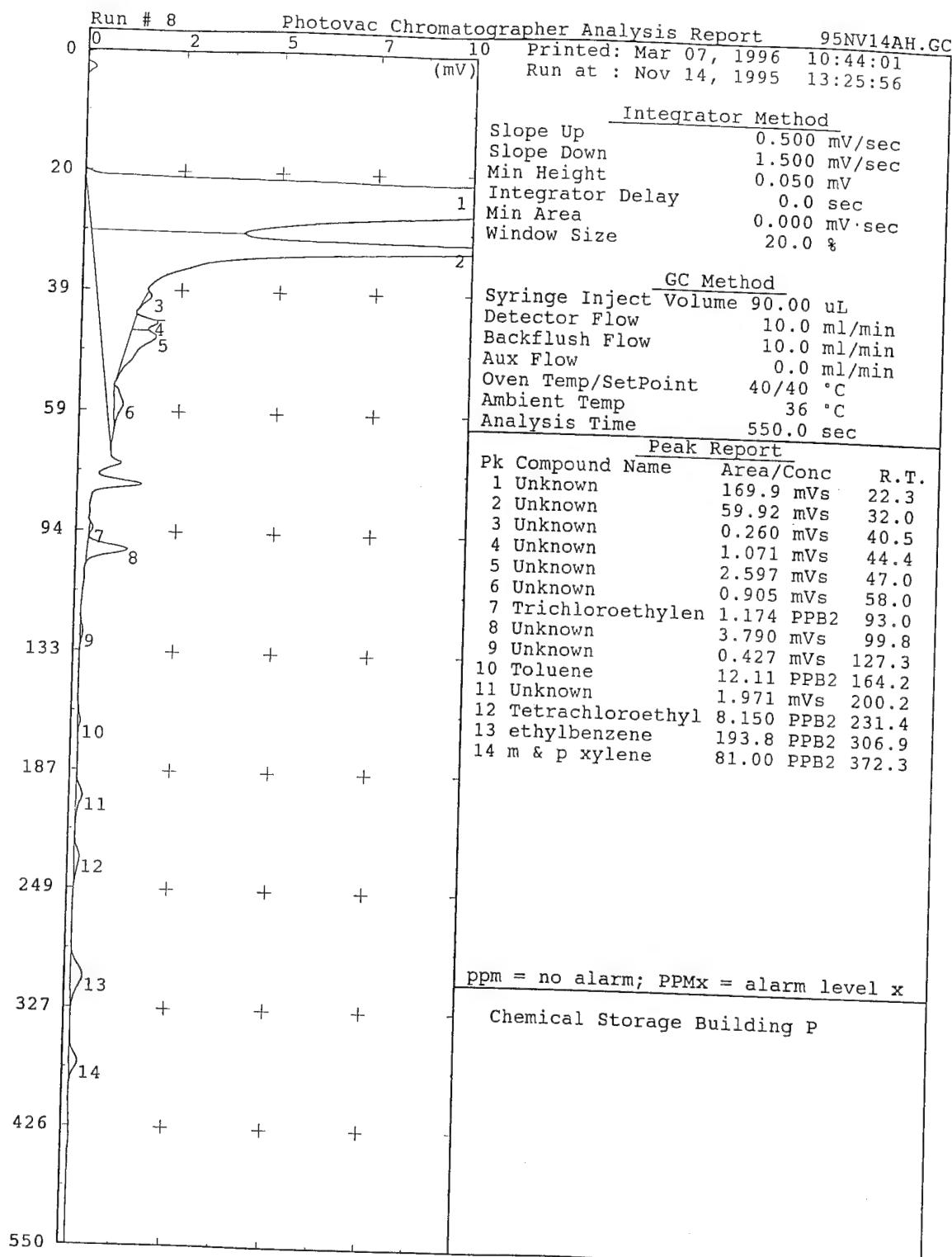


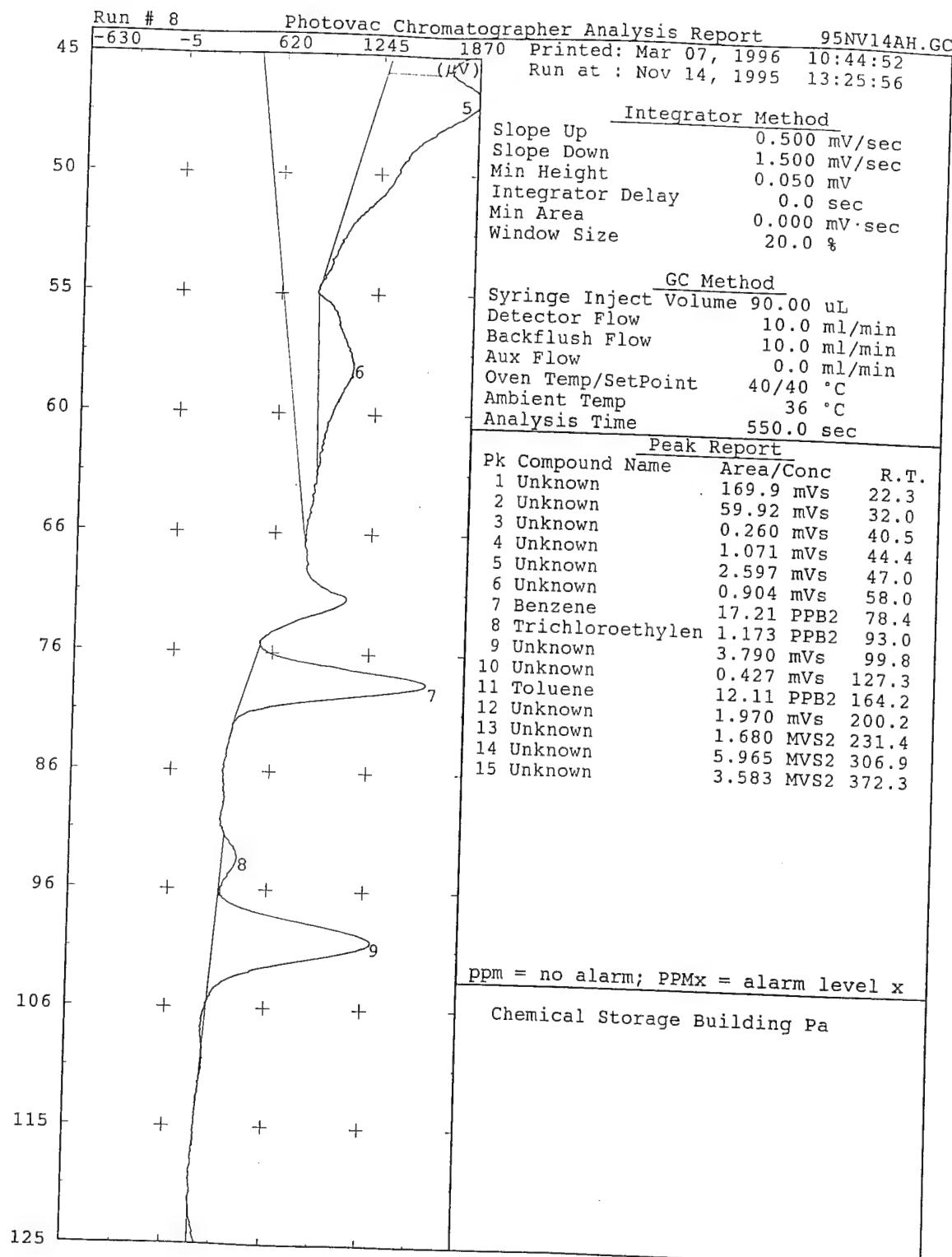


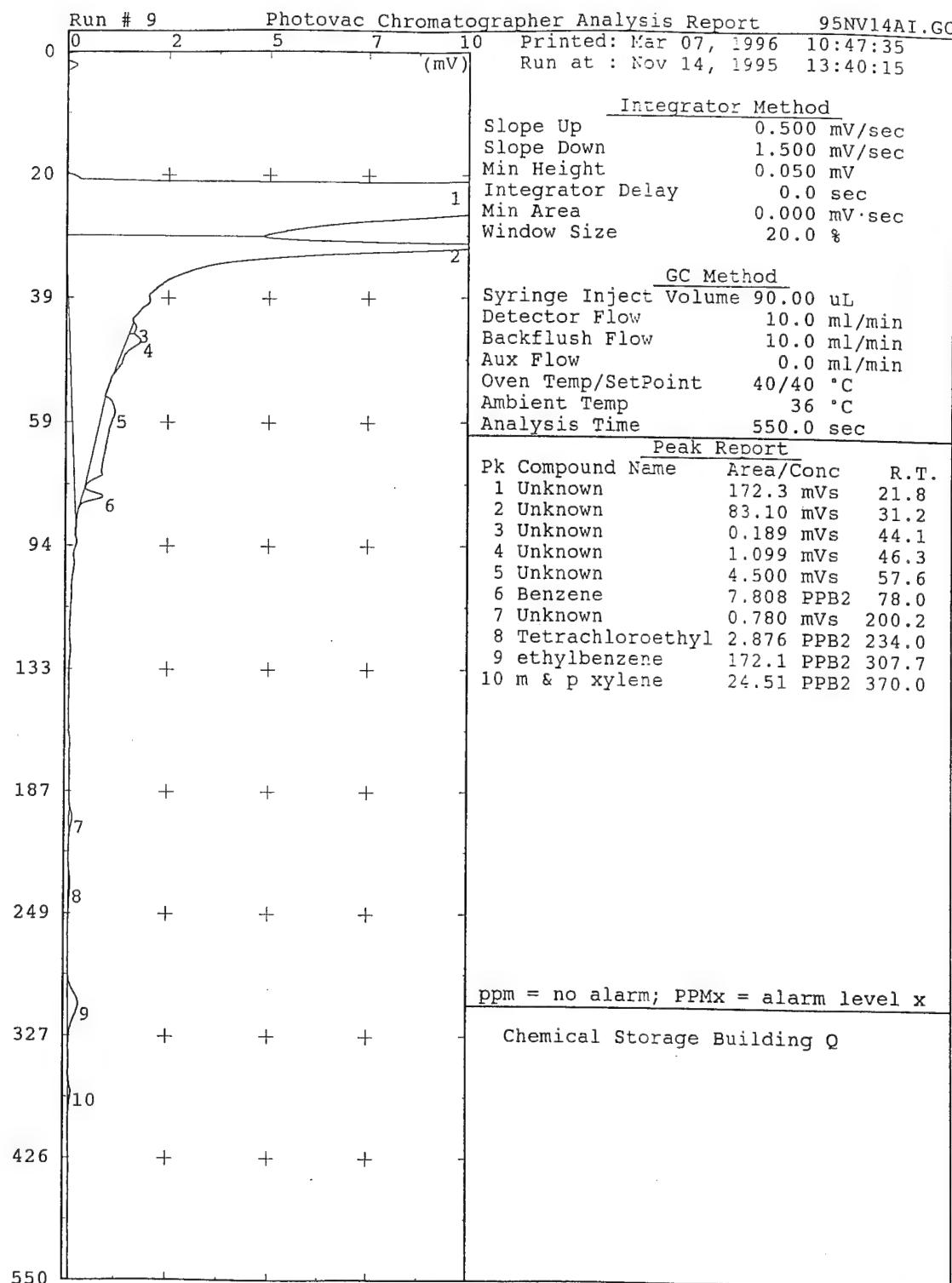


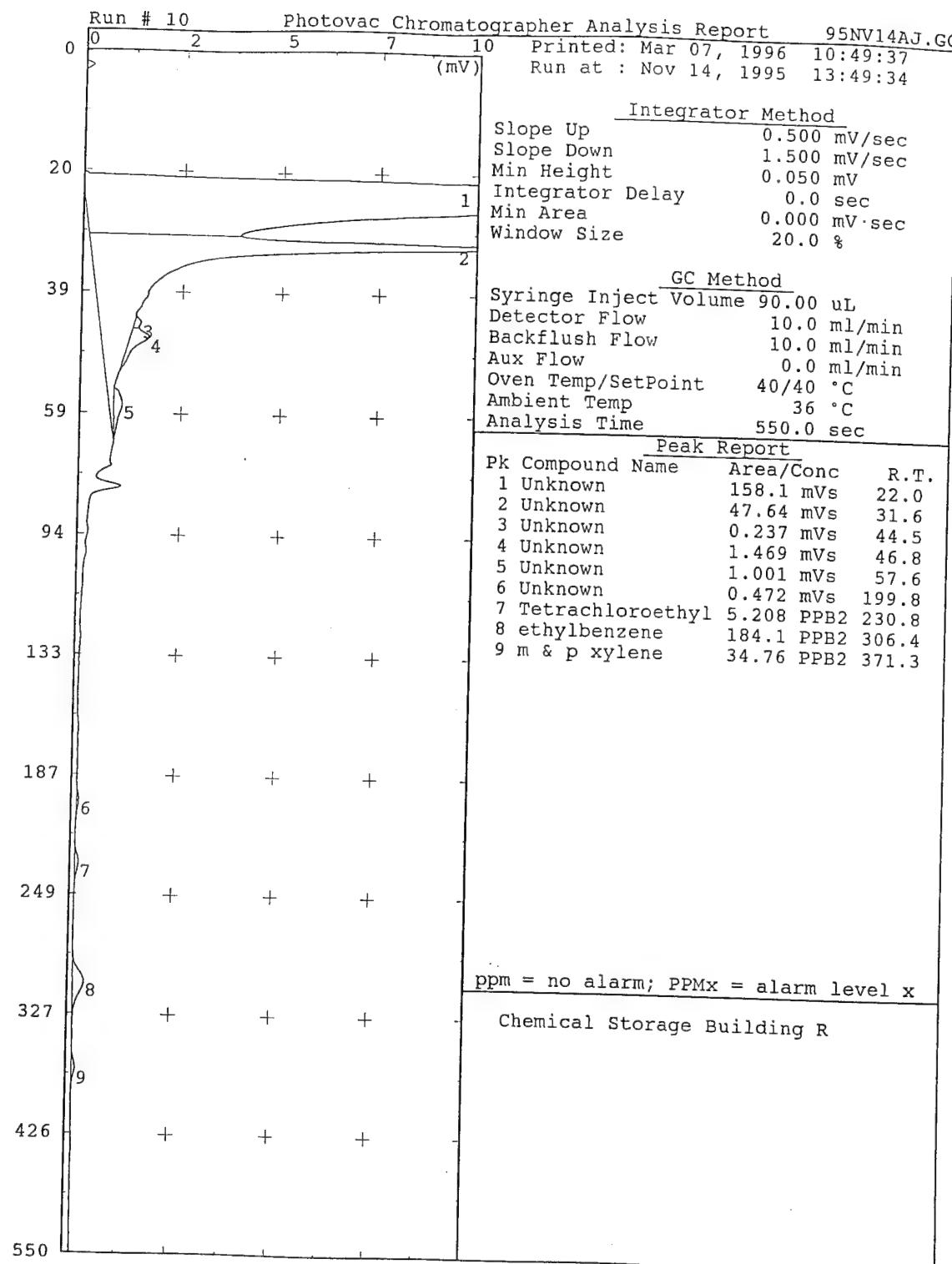


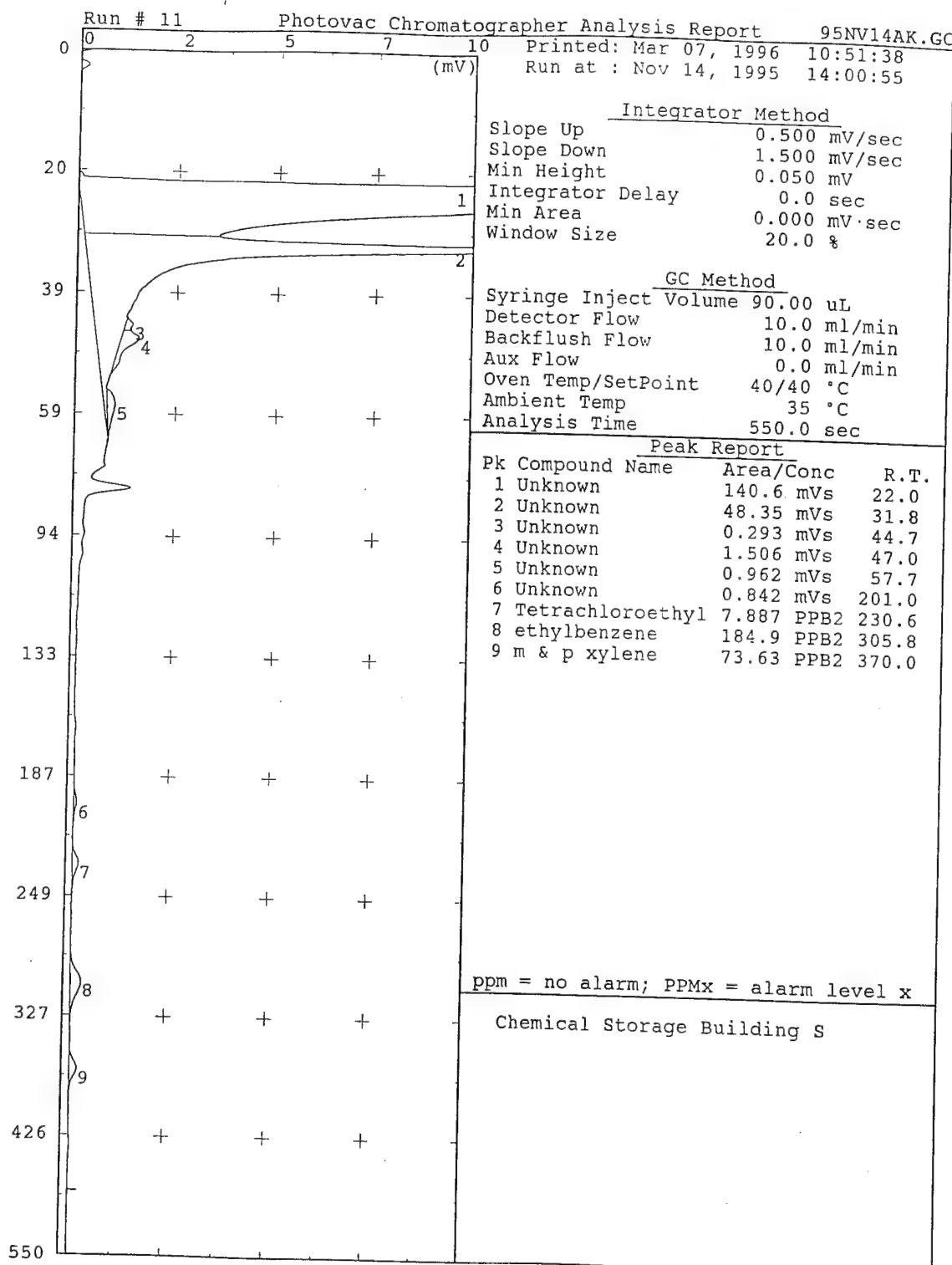


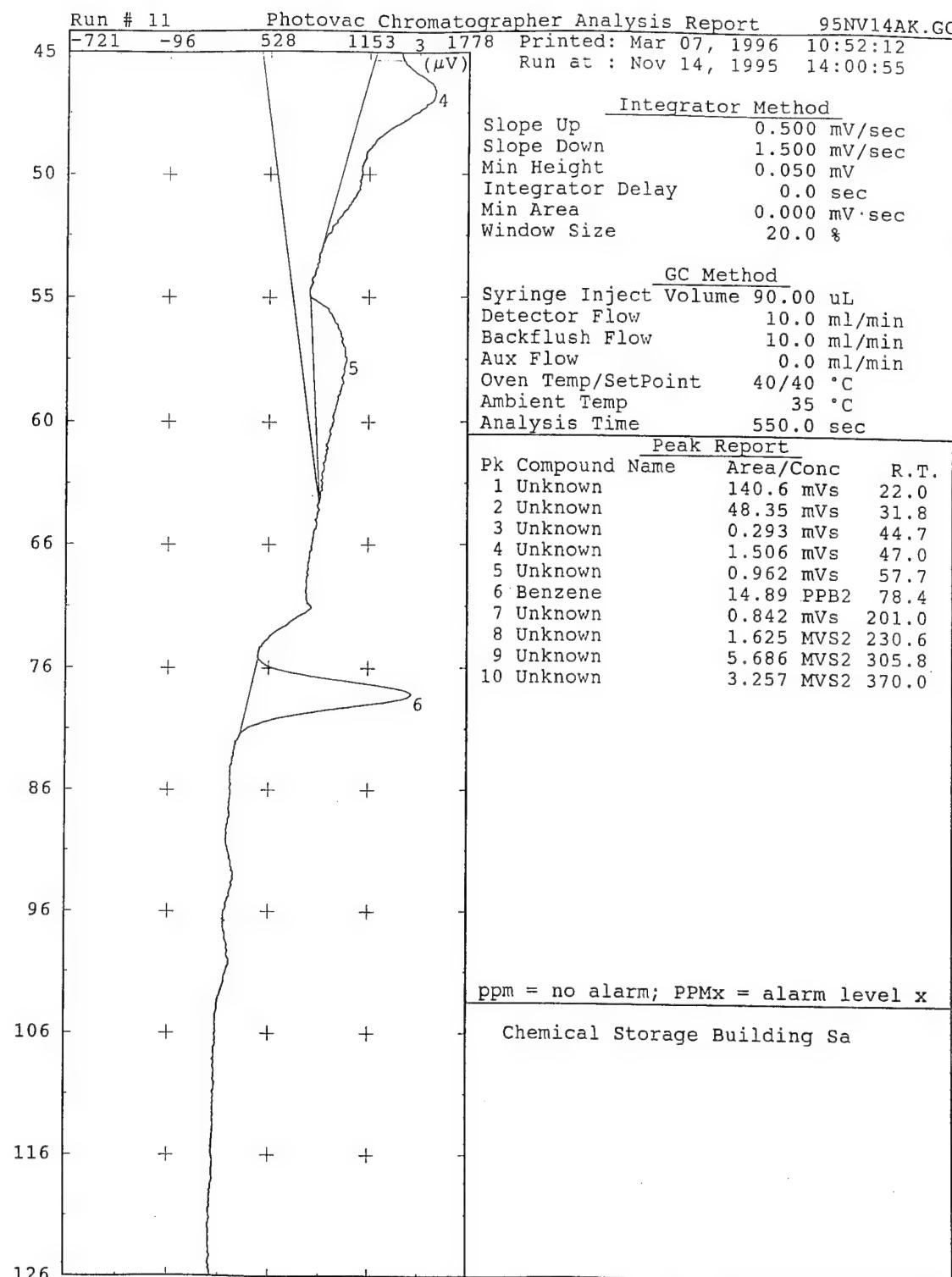


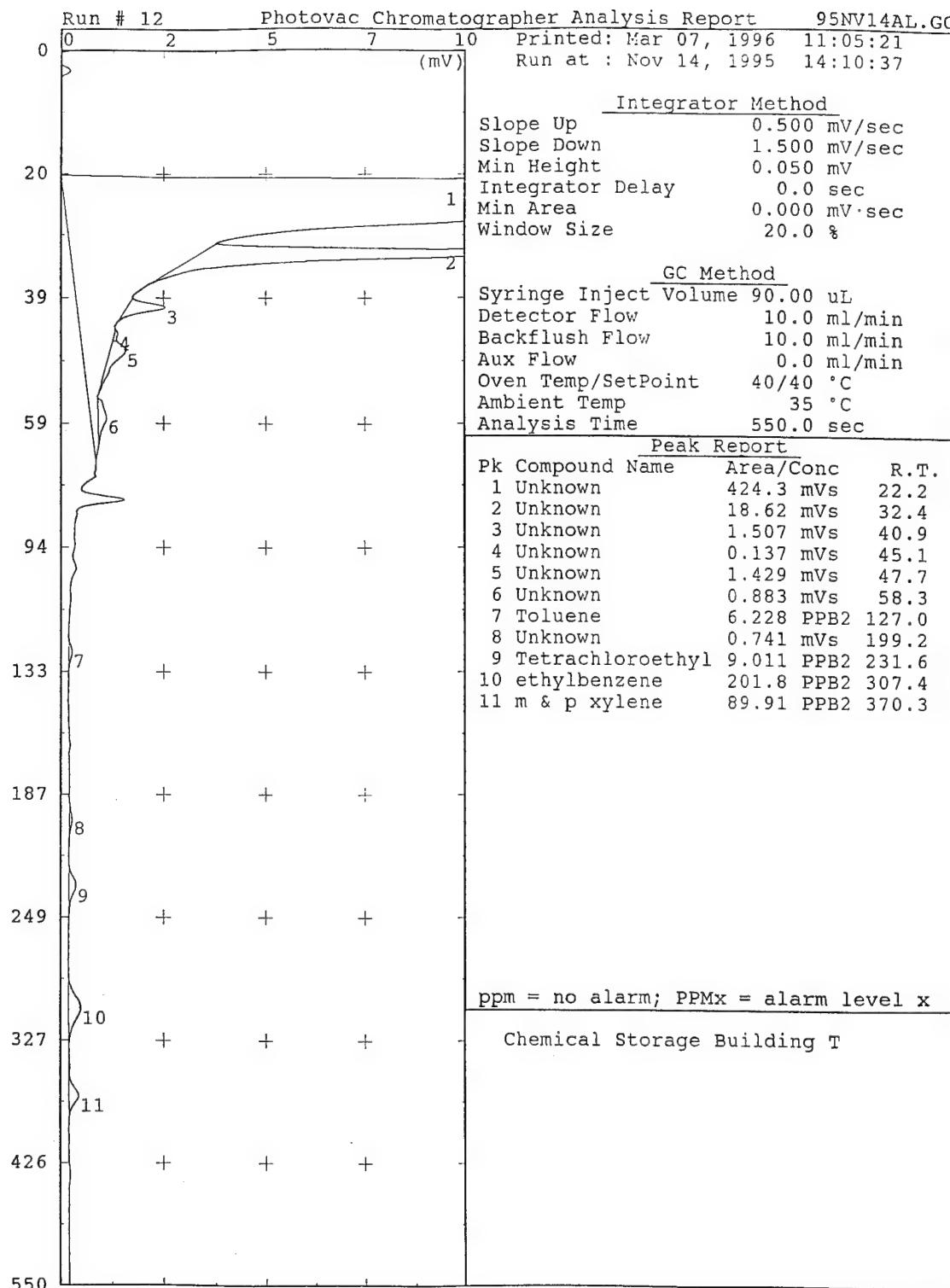


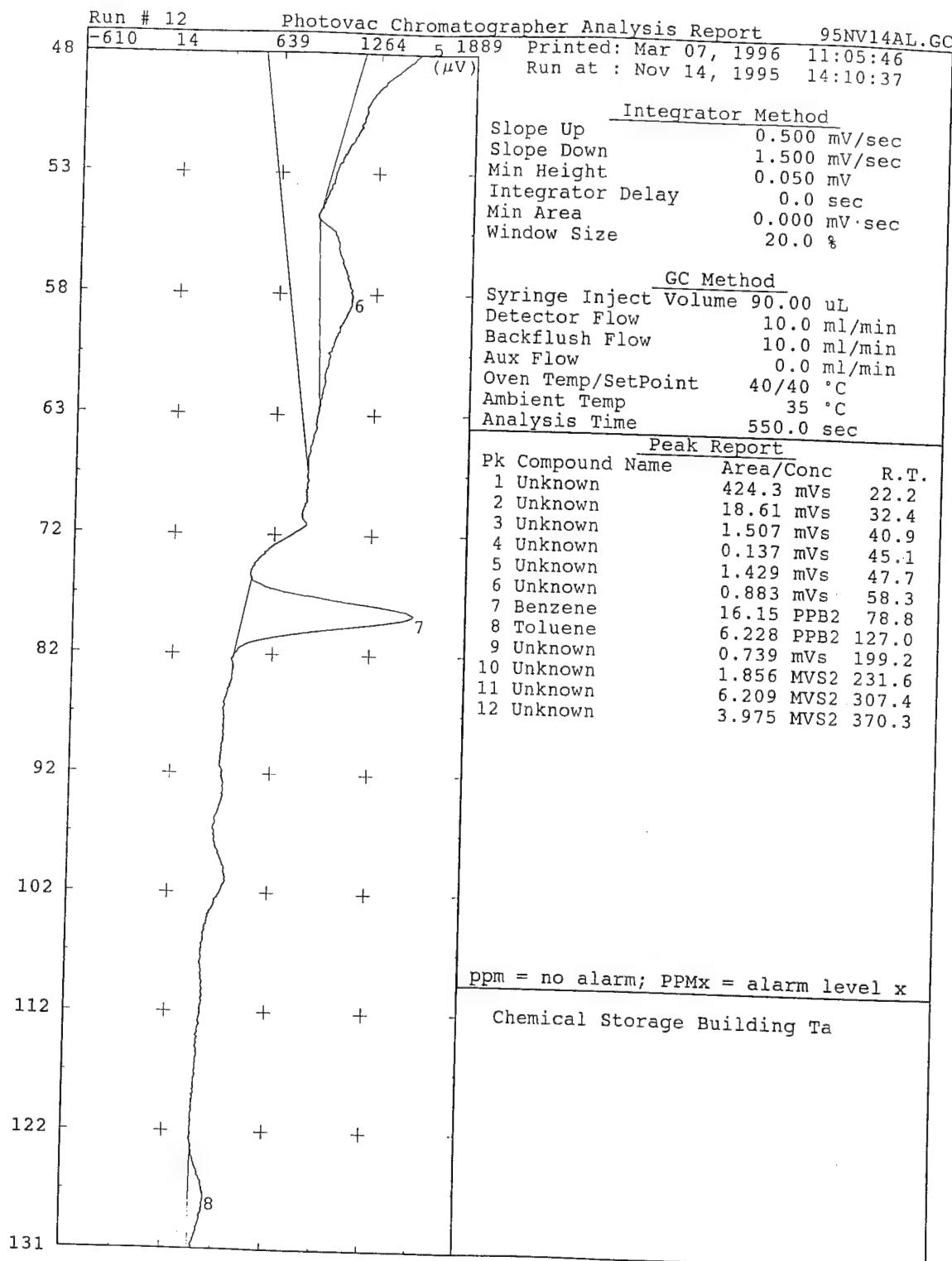


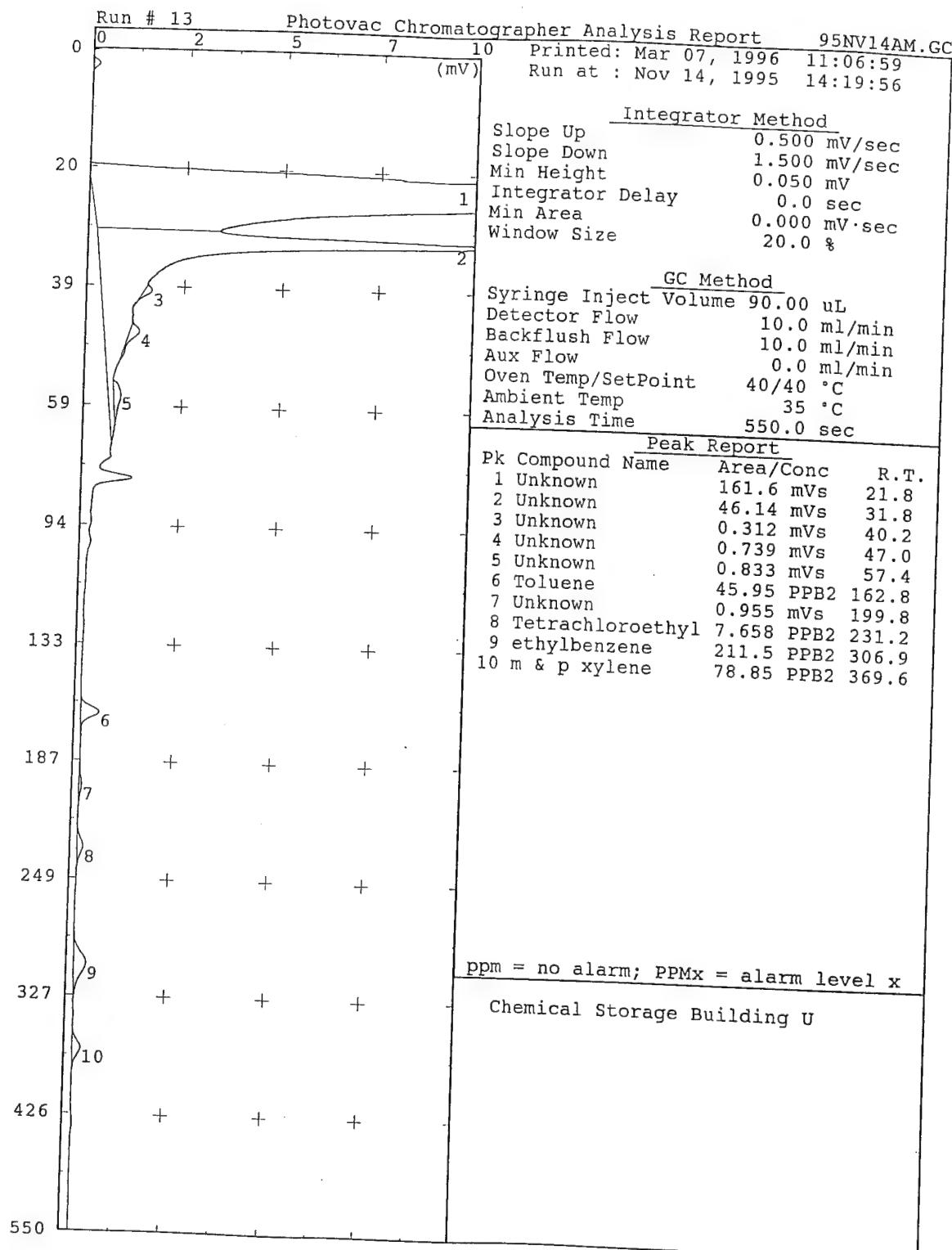


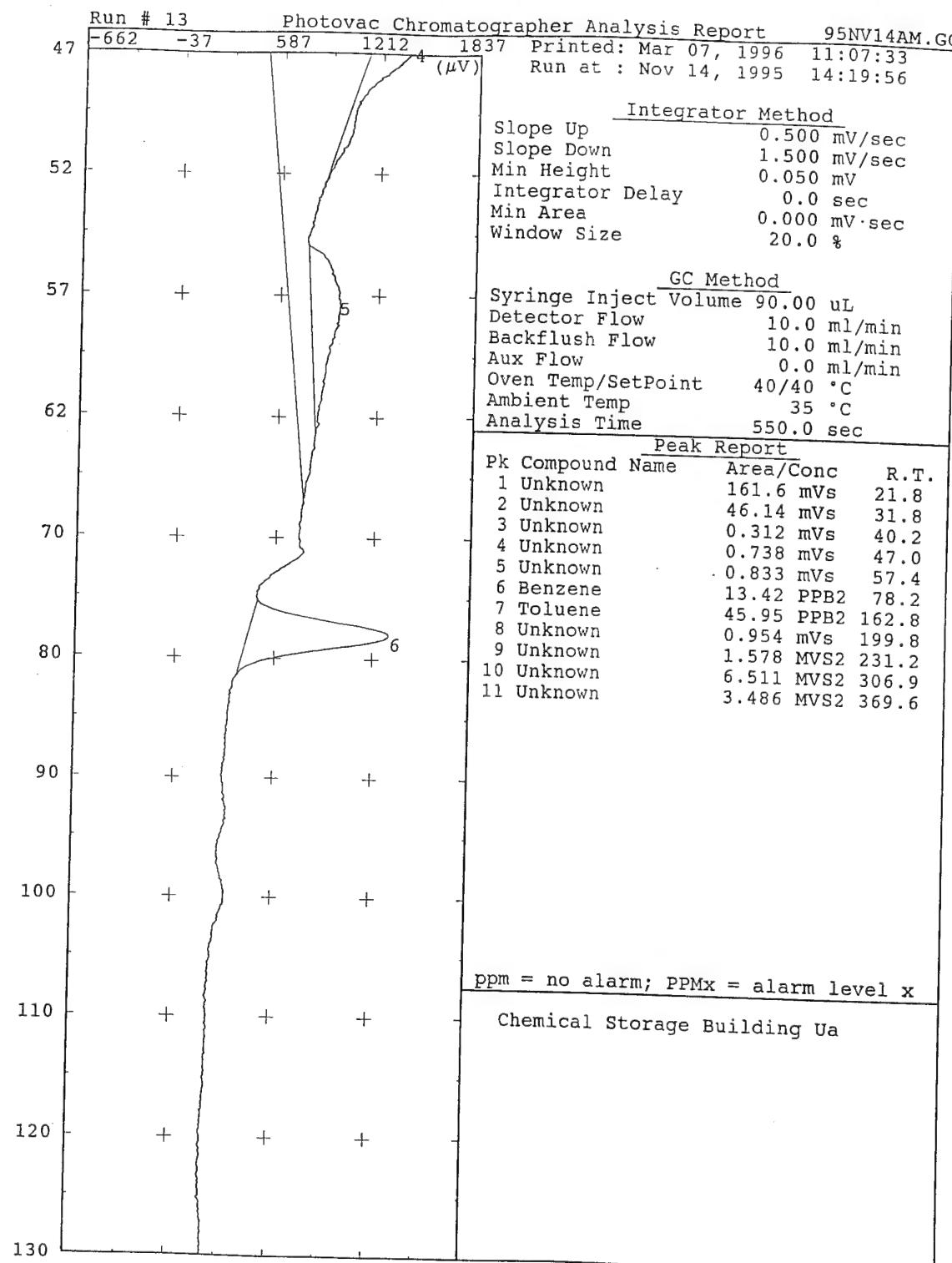


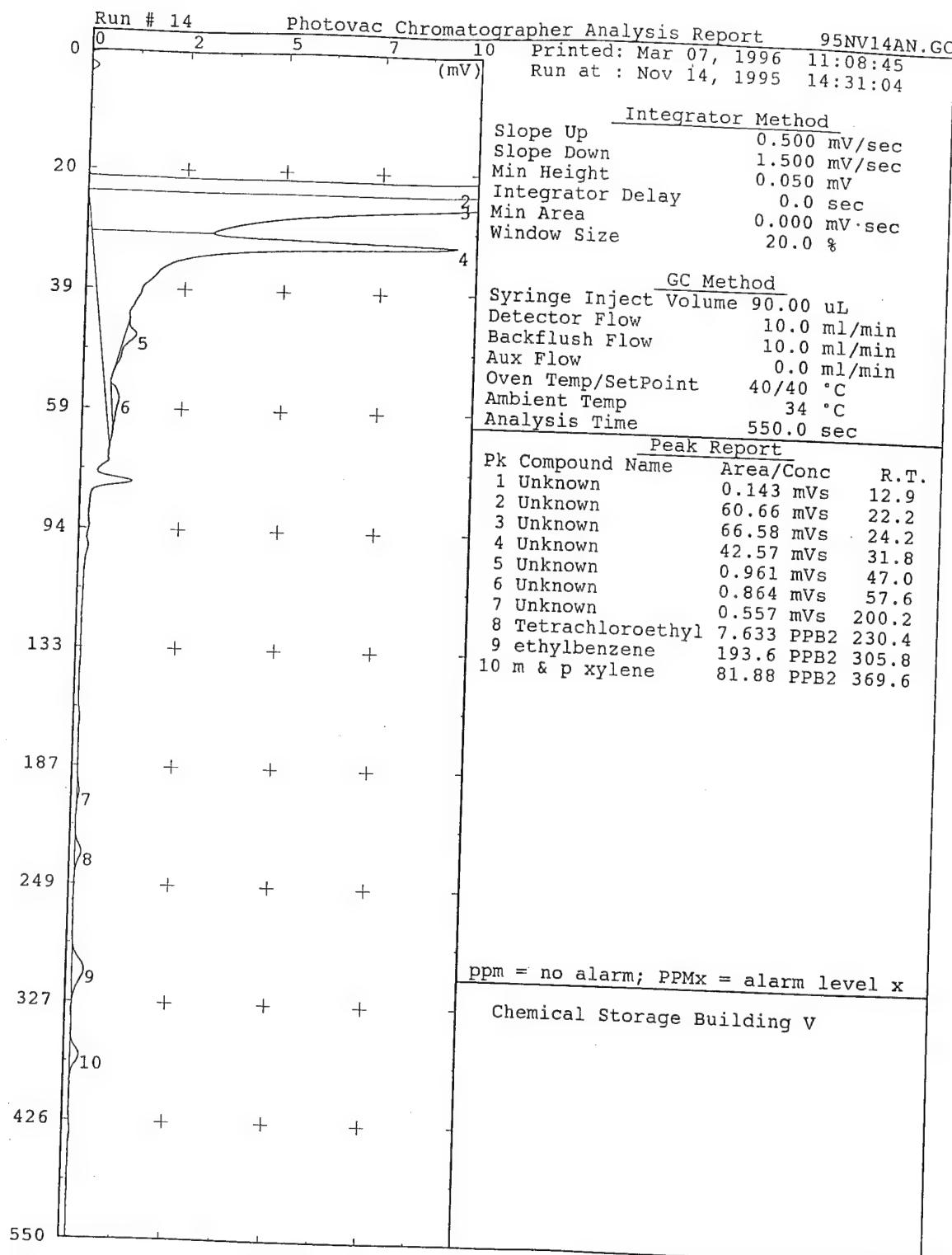


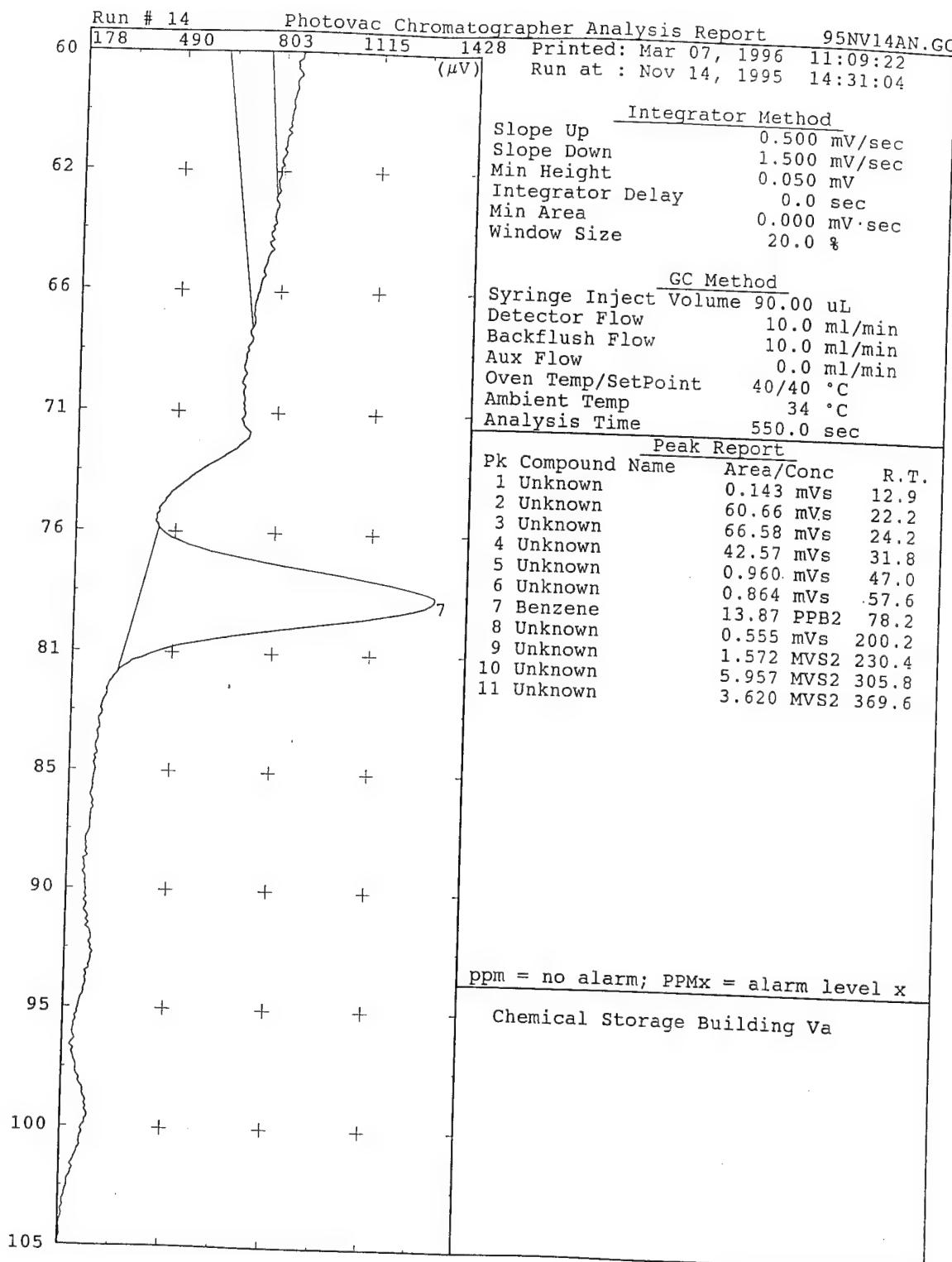


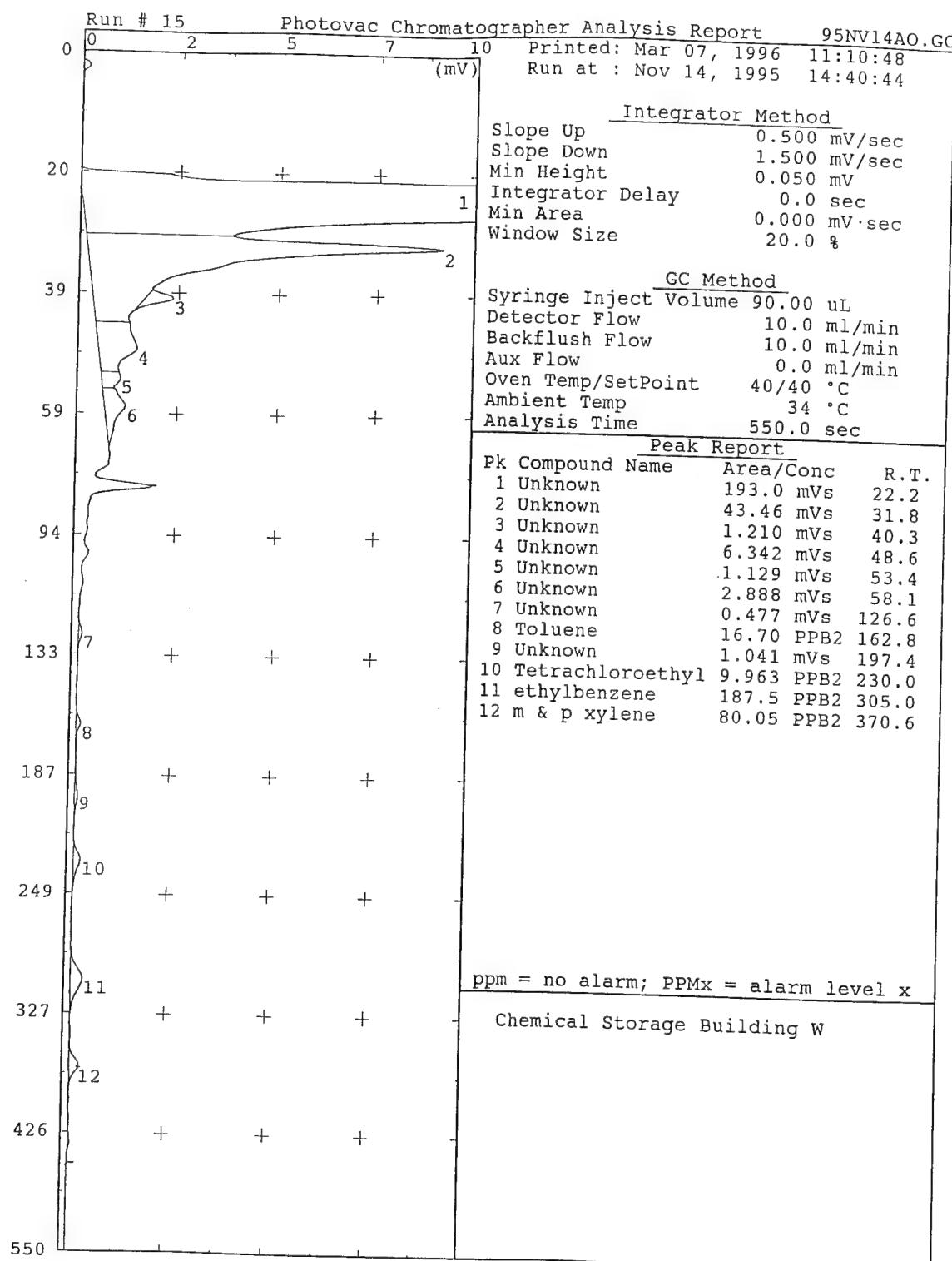


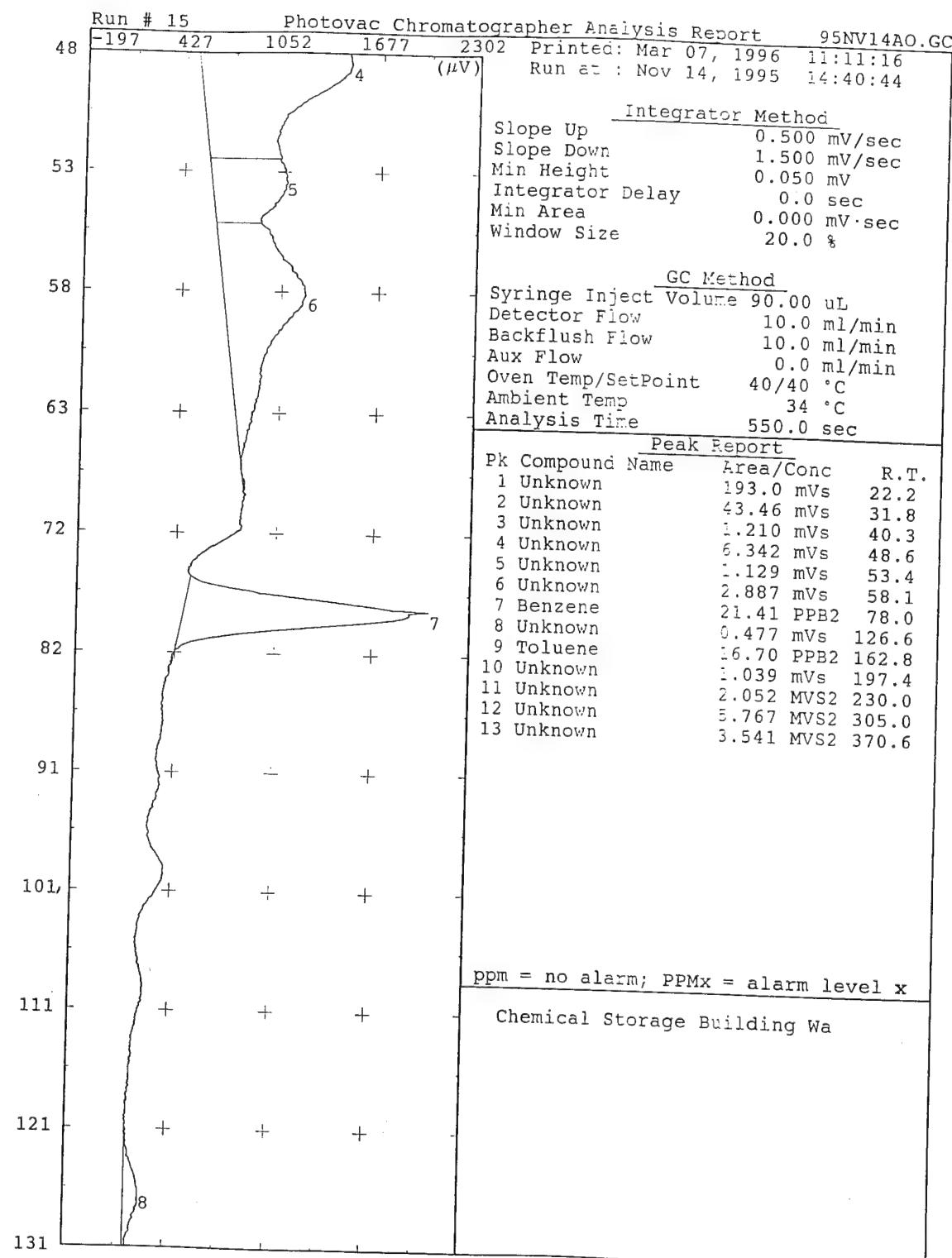












**APPENDIX F****BONFIRE SITE CHROMATOGRAMS**

